SG

ANALYTICAL ABSTRACTS

Dealing with all branches of Analytical Chemistry: Published Monthly with THE ANALYST by the Society for Analytical Chemistry

Editor: NORMAN EVERS, B.Sc., Ph.D., F.R.I.C.
14, BELGRAVE SQUARE, LONDON, S.W.1
Telephone: BELgravia 3258

Published for the Society by
W. HEFFER & SONS, LTD., CAMBRIDGE, ENGLAND

Volume 5 Price 8s.
Subscription Rate, inclusive of Index, 75s. per annum, Post Free
No. 8, Abstracts 2478-2866 August, 1958

IMPORTANT NOTICE TO SUBSCRIBERS

(Other than Members of the Society)

The Subscription to *Analytical Abstracts*, inclusive of Index, is £3 15s. per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes is £6 6s. per annum.

Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost is £4 10s. per annum, exclusive of Index.

The price of single copies of *Analytical Abstracts*, including back numbers, is 8s. post free.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.

IMPORTANT NOTICE TO SUBSCRIBERS

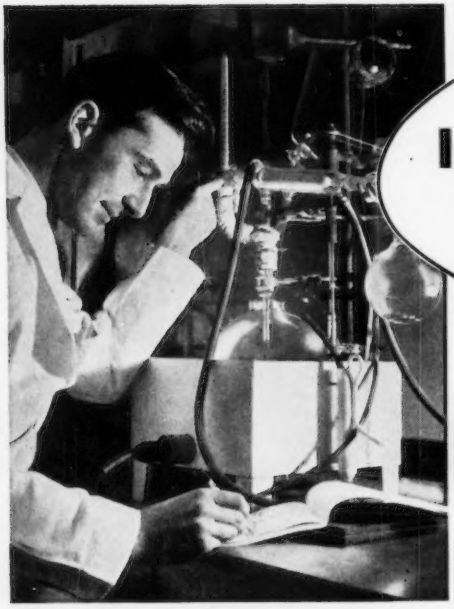
(Other than Members of the Society)

The Subscription to *Analytical Abstracts*, inclusive of Index, is £3 15s. per annum; and for *Analytical Abstracts* together with *The Analyst* and Indexes is £6 6s. per annum.

Analytical Abstracts is available printed on one side of the paper only, suitable for incorporation into reference systems; the cost is £4 10s. per annum, exclusive of Index.

The price of single copies of *Analytical Abstracts*, including back numbers, is 8s. post free.

All further enquiries about subscriptions should be made through the Secretary, the Society for Analytical Chemistry, 14, Belgrave Square, London, S.W.1. Telephone: BELgravia 3258.



Incidental information

No. 12

items of interest from our laboratory notebooks

The unique properties of Toluene—3 : 4—dithiol have drawn attention to the potentialities of dithiols in the analytical field. Now comes **Quinoxaline–2 : 3-dithiol** as a quantitative reagent for nickel at the 0.03 to 3.0 p.p.m. level. (**Anal. Chem.**, 1958, **30**, 365) and for the detection of Ni in qualitative analysis (R. E. D. Clark, **Analyst**, in the press). This is all very recent work but the reagent is ready (H. & W. Code 7393).

H&W

We have added so many metal indicators (for EDTA titrations) to our range since the last edition of our catalogue that we hesitate to pick on any one for special mention. The most recent was **Naphthyl Azoxine** (H. & W. Code 5959) for Cd, Co, Cu, Pb, Ni and rare earths (see **Anal. Chem.**, 1957, **29**, 821), but we have most others already in stock.

H&W

Nitrosoresorcinol monomethyl ether is a comparatively new colorimetric reagent for iron and cobalt. There are others, of course, but S. M. Peach (**Analyst**, 1956, **81**, 371) considers that this one has some particular advantages. For instance, the Co complex can be extracted into an organic solvent. The reagent will appear as an addition (H. & W. Code 6303) in our next catalogue amendment.

H&W

HOPKIN & WILLIAMS Limited

CHADWELL HEATH · ESSEX · ENGLAND

Branches in LONDON · MANCHESTER · GLASGOW Agents throughout the U.K. and all over the World

ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2478. **Modern analytical chemistry in industry.** Proceedings of the Congress held at the University of St. Andrews, June 24th to 28th, 1957. Publ. for the Society for Analytical Chemistry by W. Heffer and Sons Ltd., Cambridge, England. 241 pp. The following papers were contributed. **Analytical chemistry in industry (lecture),** J. Craik, 3–9. **Analytical research in the Department of Scientific and Industrial Research in relation to industry,** G. R. Davies, 10–20. **Modern analytical methods in the iron and steel industry,** B. Bagshawe, 21–33. **Steelworks analysis by spectrographic methods,** D. Manterfield, 34–42. **Chemical problems in the electrical industry: the contribution of analysis as a research service,** R. C. Chirnside, 43–55. **The application of physical methods of analysis in the gas industry,** A. B. Densham and G. Gough, 56–66. **The work of the Department of the Government Chemist,** G. M. Bennett, 67–71. **Analytical developments in a pharmaceutical laboratory,** D. C. Garratt, 72–81. **Analysis and food (lecture),** E. B. Hughes, 82–95. **Recent progress in separating substances of high molecular weight,** R. L. M. Synge, 96–101. **Emission spectroscopy in industrial analysis,** M. Milbourn, 102–108. **Analysis in medical research,** A. T. James, 109–118. **The analyst and infra-red spectroscopy,** A. E. Martin, 119–131. **Modern analytical chemistry in relation to the plastics industry,** J. Haslam, 132–136. **Modern analytical chemistry and the rarer metals,** A. R. Powell, 137–143. **Analytical research in the Nobel Division of Imperial Chemical Industries,** A. F. Williams, 144–160. **Process analytical control: the problems of manpower, productivity and automation,** B. W. Bradford and D. L. Nicholson, 161–168. **New analytical reagents and their applications in industrial plant-control operations (lecture),** G. F. Smith, 169–176. **The use of radioactive and stable isotopes in industrial analytical problems,** A. A. Smales and D. J. Ferrett, 177–191. **An approach to automatic analytical measurements,** D. A. Patient, 192–198. **Polarography,** G. C. Barker, G. W. C. Milner and H. I. Shalgosky, 199–218. **The application of gas chromatography in the petroleum industry,** A. I. M. Keulemans, 217–227. **The geochemical approach to prospecting for minerals,** C. F. Davidson, 228–237.

2479. **Growth of analytical chemistry in the USSR.** A. K. Babko. *Zavod. Lab.*, 1957, **23** (10), 1153–1161.—Developments during the last 40 years are reviewed. G. S. SMITH

2480. **Emission spectrographic analysis in the USSR.** V. K. Prokof'ev. *Zavod. Lab.*, 1957, **23** (10), 1187–1201.—The growth since 1930 of emission spectrographic analysis in the USSR is reviewed, and references to 129 papers are given. G. S. SMITH

2481. **Radiochemical methods of analysis in the USSR.** I. P. Alimarin. *Zavod. Lab.*, 1957, **23** (10), 1168–1171.—A short review of Russian work is presented. G. S. SMITH

2482. **Statistics in chemical analysis. I. Revealing of systematic and gross errors and the importance of accidental errors in the framework of gravimetric and titrimetric analytical procedures.** G. Gottschalk and P. Dehmel (Osram Studienges. für elektr. Beleuchtung, Berlin). *Z. anal. Chem.*, 1957, **159** (2), 81–94.—In order to evaluate an analytical procedure reliably, the systematic and gross errors must be detected and eliminated. This is illustrated by means of data from model analyses. After adjustment, an estimate of the chance error is obtained from the standard deviation, from which the fiducial limits are found by the *t*-test. J. H. WATON

2483. **Extraction separation of elements by means of easily fusible organic substances.** V. I. Kuznetsov and I. V. Seryakova (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1957, **23** (10), 1176–1180.—By the use of dimethyl sebacate (m.p. $\simeq$ 30°), a satisfactory extraction (distribution coeff. 130) of $FeCl_3$ from 10 *N* HCl is obtained, but dimethyl DL-tartrate is ineffective (distribution coeff. 0·1). Other examples show that, in general, esters of hydroxy acids are much less effective for extraction of $FeCl_3$ than esters of acids not containing hydroxyl groups. The results of experiments on the extraction of various ions from acid soln. (0·3 *N* HCl) containing ammonium halides or thiocyanate by means of diphenylamine, 1-naphthylamine and *p*-toluidine are given. The most suitable material is 1-naphthylamine, which extracts various elements in the form of complex anions, *e.g.*, CdI_4^{2-}, HgI_4^{2-} and $Zn(SCN)_4^{2-}$. To separate small amounts of Co from large amounts of Cu, the nitrate soln. of the sample containing 100 to 150 mg of Cu is evaporated to dryness, and the residue is dissolved in 1·5 ml of 0·2 *N* HCl. The soln. is mixed with 3 ml of 20% NH_4Br or KBr soln. and 2 drops of 20% NH_4I or KI soln. and then with $\simeq$ 1 g of 1-naphthylamine. The mixture is heated and the product is shaken when the amine has melted. After cooling, the aq. liquid is poured off, the amine is washed with 0·5 to 1 ml of water, and the combined water soln. is again treated with 1-naphthylamine. The operation is repeated until the amine no longer shows a blue colour due to the presence of Cu. The aq. soln. containing the Co are evaporated to dryness and the residue is ignited. Cobalt is determined by means of nitroso-R salt. The use of mixtures of amyl acetate and stearic acid and others is also studied. G. S. SMITH

2484. **Accurate measurement of pH. III. Discussion of examples.** G. Mattock (Electronic Instruments Ltd., Richmond, Surrey, England). *Lab. Practice*, 1957, **6** (10), 577–580.—Examples

are discussed that show some of the applications of pH measurements. These include the determination of concn. or activities, as illustrated by hydrolysis studies; the enquiry into the state of soln., as illustrated by the pH of blood and of sea water; and the following of kinetic processes.
J. H. WATON

2485. **Test for stability of aqueous sodium tetraphenylboron solutions.** S. S. Cooper (Dept. of Chem., Saint Louis Univ., Mo., U.S.A.). *Chemist Analyst*, 1957, **46** (3), 62–64.—The mol. extinction coeff. a_M of a soln. is given by $A_S = a_M bc$, where A_S is the extinction, b is the light-path length in the soln., c is the molar concn. The value for a_M at a given wavelength is const. for each constituent of the soln., but may be taken as a combination of values of more than one component if the i.r. absorption characteristics are not different at the fixed wavelengths. A_S at a single wavelength could serve as a stability test if c were known for a stable reference soln. and the test soln. Measurements at two wavelengths enable the terms c and b to be cancelled, giving $A_{S1}/A_{S2} = K$, which may be determined for a stable soln. and compared with the value for a test soln. as a stability test. With a Beckman DU spectrophotometer, A_S was determined for stable (pH 8 to 9) soln. of sodium tetraphenylboron at 2500 A and 2700 A, and the values were divided by A_S at 2625 A, which is a critical wavelength for stable soln. Graphs of A_S *vs.* wavelength and K *vs.* wavelength, and a Table, show which soln. were stable or unstable. Dil. soln. (1×10^{-4} *M*) of sodium tetraphenylboron should be made alkaline to ensure stability.
R. L. MORTLOCK

2486. **Nature of Bindschedler's green. Preparation for analysis of hydrazo compounds.** H. J. Shine, R. L. Snell and J. C. Trisler (Texas Technol. College, Lubbock, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 383–384.—Bindschedler's green, when prepared by a modification of Wieland's method (*Ber.*, 1915, **48**, 1078), is stable for long periods of time and generally gives clear, colourless end-points in titrations with $TiCl_3$. A simple method is given for the preparation of the red form of the reagent. Both forms are discussed and the structures and equivalent weights are given from analytical data.
G. P. COOK

2487. **Calculation of titration curves.** F. H. C. Barkhuysen. *Chem. Weekbl.*, 1957, **53** (44), 590–596.—Eight equations representing the concn. of ionic and molecular species present during the titration of a tribasic acid with a monoacidic base are solved for $[H^+]$, yielding a basic 6th order equation in powers of $[H^+]$. Values for the coefficients are derived in terms of the equilibrium constants. Hence equivalence points and titration curves can be calculated for the titration of mono-, di- and tri-basic acids, both weak and strong, by a weak or strong base. Alternatively, dissociation constants can be calculated from an empirical titration curve. The titration of mixtures of polybasic acids is discussed.
G. BURGER

2488. **Iodimetry in ultra-violet light.** K. P. Stolyarov. *Uch. Zap. LGU*, 1957, (211), 92–104; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,306.—An earlier method for determining the equivalence point without the use of an indicator, by the disappearance of the shadow on a fluorescent screen when observing in u.v. light, is used for the iodimetric determination of iodine, IO_3^-, BrO_3^-, SO_3^{2-}, $S_2O_3^{2-}$, H_2O_2, H^+, oxalic acid, As^{3+}, Cr^{6+}, Fe^{3+}, Cu^{2+}, Ba and Pb. In all cases the fluorescent screens were glass plates covered with a thin layer of a phosphor, the luminescence of which was excited by u.v. light of wavelength 365 mμ. The method enables more accurate results to be obtained. It is established that in several iodimetric determinations (H_2O_2, IO_3^-, HCl, $Cr_2O_7^{2-}$, CrO_4^{2-}) it is expedient to use ascorbic acid instead of $Na_2S_2O_3$.
C. D. KOPKIN

2489. **The oxidising action of N-bromosuccinimide.** A. Berka and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1957, **51** (10), 1823–1827.—The oxidising action of 0·01 *M* soln. of N-bromosuccinimide (**I**) on various inorganic and simple organic systems has been studied with the use of potentiometric or visual indication. It has been found that, with the use of **I**, the following oxidimetric determinations can be carried out—As^{3+} (0·1 to 15 mg, in 0·05 *N* NaOH to 18% HCl), Sb^{3+} (0·3 to 20 mg, in 12% HCl), Sn^{2+} (2 to 15 mg, in 2% HCl), Ti^{3+} (2 to 15 mg, in 15% HCl), Tl^+ (5 to 20 mg, in 10% H_2SO_4), I^- (0·2 to 10 mg, in 13 to 18% HCl), iodine (5 to 15 mg, in 15% HCl), SCN^- (2 to 20 mg, in $NaHCO_3$ soln.), S^{2-} (2 to 15 mg, in soln. of pH 5 to 7), quinol (2 to 15 mg, in neutral soln. or in 3% HCl), quinhydrone (5 to 20 mg, in neutral soln. or in 3% HCl), hydrazine (0·3 to 3 mg, in neutral soln. or in 5% HCl), and thiourea (0·4 to 5 mg, in $NaHCO_3$ soln.). The disadvantage of **I** is the low stability of its soln. The action of **I** is compared with that of other reagents containing bromine as an essential constituent.
J. ZÝKA

2490. **Spectrophotometric titrations with alkaline ferricyanide as a volumetric oxidising agent.** M. G. Bapat and S. V. Tatwawadi (Hindu Univ., Benares). *Naturwissenschaften*, 1957, **44** (21), 557–558 (in English).—Changes in the colour of alkaline $K_3Fe(CN)_6$ can be registered with the Hilger Spekker absorptiometer (filter 450 to 480 mμ) and thus be self-indicating in oxidimetric titrations. When a weighed amount of $K_3Fe(CN)_6$ is titrated in 10 to 15% NaOH or KOH soln. with arsenous oxide, the end-point is shown by a minimum value in the colour (absorptiometer reading) which is not changed by adding an excess. Hydrazine sulphate can be determined by this method provided that small amounts of osmium tetroxide are present to act as catalyst. Selenous acid can be determined with an accuracy of $\pm 1\%$ in 0·001 *M* concn. if taken through an indirect iodimetric titration in the presence of thiosulphate, with subsequent alkaline ferricyanide titration of the thiosulphate.
E. KAWERAU

2491. **The EDTA titration: nature and methods of end-point detection. IV.** A. J. Barnard, jun., W. C. Broad and H. Flaschka (J. T. Baker Chem. Co., Phillipsburg, N.J., U.S.A.). *Chemist Analyst*, 1957, **46** (3), 76–84.—A detailed review is given of possible redox indicators. Methods are described for detecting titration end-points by photometry with or without indicators, thermochemical effects, electrometry, chronopotentiometry, amperometry, conductimetry, high-frequency conductivity and coulometry. (*Cf. Anal. Abstr.*, 1957, **4**, 2073; 1958, **5**, 1432, 2492.) (227 references.) R. L. MORTLOCK

2492. **The EDTA titration: Applications. I.** H. Flaschka, A. J. Barnard, jun., and W. C. Broad (Univ. of North Carolina, Chapel Hill, U.S.A.).

Chemist Analyst, 1957, **46** (4), 106–112.—Applications to the determination of various cations and anions, water hardness, organic compounds, pharmaceuticals and biological fluids are reviewed.
G. S. ROBERTS

2493. **A summary of known conditions for visual EDTA titration.** R. W. Schmid and C. N. Reilley (Dept. Chem., Univ. N. Carolina, Chapel Hill, N.C., U.S.A.). "The EDTA Titration," publ. by J. T. Baker Chem. Co., Phillipsburg, N.J., 1957, 30 pp.—Many of the indicators reported for the visual EDTA titration of some important metals are listed with titration conditions, end-point colour change and literature references. It is also noted whether a direct or a back-titration is involved.
N. E.

2494. **Complexometric titrations (chelatometry). XXXIII. Primary standards in chelatometry.** J. Vrešťál, J. Havíř, J. Brandštetr and S. Kotrlý (Military Tech. Acad., Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (11), 2023–2031.—Various known and some new primary standards were examined for use as volumetric agents in chelatometry by the determination of the EDTA factor; murexide, Eriochrome black T, catechol violet and xylenol orange were used as indicators. The following primary standards were studied—metallic Cu, Ni, Bi, Zn and Cd, ZnO, PbO, $PbCl_2$, $Pb(NO_3)_2$, $ZnSO_4.7H_2O$, $(NH_4)_2Mg(SO_4)_2.6H_2O$, $(NH_4)_2Cd(SO_4)_2.6H_2O$, $Cd(IO_3)_2.H_2O$, $Cd(C_5H_5N)_2(SCN)_2$, $Zn(C_5H_5N)_2(SCN)_2$ and Cd anthranilate. Of these, $PbCl_2$ was found to be the most suitable primary standard for chelatometric determinations.
J. ZÝKA

2495. **Metallochromic indicators. VI. Analogues of "o-cresolphthalein complexone."** J. Körbl and R. Přibil (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1957, **51** (10), 1804–1808.—The acido-basic and metallochromic properties of 3:3′-bis-NN-di(carboxymethyl)aminomethyl derivatives of phenolphthalein, *o*-cresolphthalein and thymolphthalein are compared, and the use of these compounds as indicators in complexometric titrations of Ca, Sr and Ba is described.

VII. Glycinethymol blue. J. Körbl, E. Kraus and R. Přibil. *Ibid.*, 1957, **51** (10), 1809–1813.—The metallochromic properties of 3:3′-di-(N-carboxymethylaminomethyl)thymolsulphonephthalein (glycinethymol blue) (**I**) are described. **I** has been found to be a suitable and specific indicator for the complexometric determination of Cu in acid medium. *Procedure*—Dilute a measured vol. of 0·05 *M* $CuSO_4$ to 100 ml, add *N* HNO_3 (1 ml), indicator (0·1% soln. of the sodium salt of **I** in H_2O) (5 to 10 drops) and hexamine (20%) (3 ml) and titrate with 0·05 *M* EDTA (disodium salt) till the blue colour of the soln. is discharged. The resulting soln. is yellow or emerald green, according to the amount of Cu. The complexometric titration of Co, Pb, Zn, Hg and Cd in slightly alkaline soln. with the use of **I** as indicator is also possible, but has no advantages.
J. ZÝKA

2496. **Some further applications of xylenol orange as an indicator in the EDTA titration.** J. Kinnunen and B. Wennerstrand (Outokumpu Oy, Metalworks, Pori, Finland). *Chemist Analyst*, 1957, **46** (4), 92–93.—Brief details are given of the determination of Tl^{III}, In, Ga, Fe^{III}, Ni, Co, Cu^{II}, U^{IV}, V, Cr, Ti, rare-earth metals, Y, Sc, Zr, Hf, Al (in slags and silicates), Sn (in bronze) and PO_4^{3-}.
G. S. ROBERTS

2497. **Some oo′-dihydroxyazo indicator dyes for EDTA titrations.** R. Belcher, R. A. Close and T. S. West (Univ., Birmingham, England). *Chemist Analyst*, 1957, **46** (4), 86–88.—The results obtained in the study of commercial dyestuffs related to C.I. 203 (Eriochrome black T) as indicators for EDTA titrations are reviewed.
G. S. ROBERTS

2498. **A new group of metallochromic indicators.** J. Körbl, V. Svoboda, D. Terzijská and R. Přibil (Res. Inst. Pharm. and Biochem., Czech. Acad. Sci., Prague). *Chem. & Ind.*, 1957, (50), 1624–1625.—A series of 3:3′-biscarboxymethylaminomethyl derivatives of thymol- and *o*-cresolsulphonephthalein, thymol- and *o*-cresol-phthalein, and fluorescein have been prepared by condensation methods analogous to those described previously (*cf.* Körbl and Přibil, *Anal. Abstr.*, 1957, **8**, 2477). Eighteen of these derivatives (including glycinethymol blue) are listed and their characteristics as possible metallochromic indicators (especially for Cu^{2+} and Ni^{2+}) are reviewed briefly. (*Cf. Anal. Abstr.*, 1958, **5**, 2495.)
W. J. BAKER

2499. **Eriochrome cyanine as an indicator in chelatometry.** C. Manoliu. *Rev. Chim., Bucharest*, 1957, **8** (11), 716–718.—This indicator replaces Eriochrome black T in titrations with EDTA for the determination of Mg, and of Mg in the presence of Ca. It can also be used instead of murexide in the determination of Cu^{2+} and instead of sulphosalicylic acid in the determination of Fe^{3+}.
H. SHER

2500. **Resazurin ethyl ether and resorufin ethyl ether as stannimetric redox indicators.** E. Ružička (High Pedagog. School, Olomouc, Czechoslovakia). *Chem. Listy*, 1957, **51** (10), 1814–1818.—The redox potentials of resazurin ethyl ether and resorufin ethyl ether were measured, and both compounds were found to be suitable indicators for the stannimetric determination of OsO_4, $Cr_2O_7^{2-}$, $Fe(CN)_6^{3-}$, VO_3^-, Fe^{3+}, $PtCl_6^{2-}$ and Ir^{4+} in HCl soln. The following amounts of HCl were used for the titration of 10 ml of the soln.—$Cr_2O_7^{2-}$ (2 ml of 4 *N* HCl, colour change brown - red to green - blue), $Fe(CN)_6^{3-}$ (5 ml of 12 *N* HCl, colour change red to green - blue), VO_3^- (2 ml of 4 *N* HCl, colour change red to green - blue), $PtCl_6^{2-}$ (5 ml of 12 *N* HCl, colour change red to green), Ir^{4+} (10 ml of 12 *N* HCl, at 80°, colour change brown - red to green - blue), OsO_4 (10 ml of 12 *N* HCl, colour change brown - red to green), Fe^{3+} (5 ml of conc. HCl, at 80°, colour change red to green - blue). There is no interference from Ni, Co, Al, Zn and Cd, but Sb^{3+}, Cu^{2+}, halogens and ions with oxidising properties must be absent.
J. ZÝKA

2501. **Conductimetric titration.** K. Trobisch (Inst. für Elektrochemie, Tech. Hochschule, Dresden). *Chem. Tech., Berlin*, 1957, **9** (11), 649–654.—The nature, advantages, and methods of conductimetric titration analysis, including automatic methods, are reviewed, and published methods, under the headings redox, pptn. and complex formation, and acidimetric titration, are summarised in tabular form. (76 references.)
J. L. PROSSER

2502. **Potentiometric titrations in non-aqueous solution. III. Directions for choosing solvent - titrant combinations.** H. B. van der Heijde (Koninklijke/Shell Lab., Amsterdam). *Anal. Chim. Acta*, 1957, **17** (5), 512–521 (in English).—Recommended solvents and titrants are classified according

to their acidity and basicity. Tables based on this classification are presented by means of which suitable combinations can be selected for the titration of acids and bases. The principles involved are discussed. G. BURGER

2503. **Examples of titrations of aprotic acids (Lewis acids).** M. Vaillant. *Chim. Anal.*, 1957, **39** (11), 413–417.—In this theoretical paper, the acid - base theories of Lewis and Brønsted are compared, and conditions are discussed for the titration of substances, such as acid anhydrides, which are acids according to the Lewis system, but not according to that of Brønsted, since they do not liberate protons. The linkages concerned are co-ordination ones, involving free doublets, and the colour changes of indicators such as azo compounds and dyes of the triphenylmethane series are discussed from this point of view. Another type of indicator is obtained from triethylaluminium, one molecule of which forms a yellow complex with one molecule, and a red complex with two molecules, of *iso*quinoline. The reverse titration procedure of Hahn (*cf. Anal. Abstr.*, 1954, **1**, 636) is advocated and the use of the yellow complex in the titration of bases other than quinoline, such as diethyl ether, is considered, together with back-titration procedures which render possible the titration of substances which react with triethylaluminium.
R. E. ESSERY

2504. **A new volatile buffer for use in chromatography and electrophoresis.** P. Fasella, C. Baglioni and C. Turano (Ist. di Chim. Biol., Univ. di Roma). *Experientia*, 1957, **13** (10), 406–407 (in Italian).—A volatile 0·5 *M* ethylenediamine - acetate buffer is described. Owing to the closeness of the boiling-points of ethylenediamine hydrate (118°) and acetic acid (118·1°), the pH remains unaltered during volatilisation. This buffer has several advantages over other volatile buffers used in chromatographic and electrophoretic procedures.
P. NICHOLLS

2505. **Infra-red spectroscopy.** G. Salomon (Centraal Lab., T.N.O., Delft). *Chem. Weekbl.*, 1957, **53** (44), 581–590.—A review. G. BURGER

2.—INORGANIC ANALYSIS

2506. **Analysis of pure metals.** V. A. Nazarenko. *Zavod. Lab.*, 1957, **23** (10), 1162–1167.—Methods for determining minute traces, 10^{-5} to 10^{-9} %, of impurities in 'pure' metals are reviewed, and 44 references, mainly to Russian work, are given.
G. S. SMITH

2507. **Paper chromatography of metal complexes. II. Replacement ability of the ligands.** A. S. Kertes (Hebrew Univ., Jerusalem). *Anal. Chim. Acta*, 1957, **17** (5), 470–475 (in English).—The R_F values on filter-paper have been measured for the compounds of Ce, La, Ca, Mg, Zn, Cd and Cu with acetic, and mono-, di- and tri-chloroacetic acids, each compound being eluted with mixtures of butanol and each of the acids in concn. from 1 *N* to 6 *N*. The results are presented and discussed. The ability of the anion in the eluent to replace the ligand in the original spot soln. is dependent on its concn., on the stability of the original complex and on the complex-forming ability of the anion in the eluent. For true interpretation of the results for complexes formed in paper chromatography, the complexing agent in the eluent should be the same as that in the original spot. G. BURGER

2508. **Use of organic reagents in inorganic analysis. V. Paper chromatography of some metal complexes of 2-hydroxy-1-nitroso-3-naphthoic acid.** Sachindra Kumar Datta and Prafullanath Ghose (Gov. College, Darjeeling, India). *Z. anal. Chem.*, 1957, **158** (5), 347–355 (in English).—The paper chromatography of soln. of the 2-hydroxy-1-nitroso-3-naphthoates of Co, Pd, U, Th and Zr in aq. NH_3 or HCl was studied. The R_F values on Whatman No. 1 paper with acetone - *iso*butyl alcohol - 12 *N* HCl (60:38:2) as developing solvent were—U 0·53, Co 0·45, Pd 0·29, Th and Zr 0·00. The use of paper impregnated with NaCl or KCl increased the mobility of the complexes, but did not lead to better separation. No other solvents were useful, nor were papers impregnated with substances other than NaCl or KCl. The positions of the complexes in the chromatograms were revealed by their colour in visible and u.v. light, alone or after application of resorcinol, NH_3 or NH_3 - alizarin reagents. A. R. ROGERS

2509. **Study of the absorption spectra of the complexones of certain metals.** I. P. Alimarin, A. P. Golovina and I. M. Gibalo. *Vestn. Moskov. Univ., Ser. Matem., Mekhan., Astron., Fiz., Khim.*, 1956, (2), 135–138; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,640.—The complex compounds of Zn, Cd, Al, Be, Hg^{2+}, Sn^{2+}, Ti^{4+}, Cr^{3+}, Ag, Mn^{2+}, Ba, Sr, Ca, Mg, Ga, Ge, Pb and Bi with EDTA (disodium salt) (**I**) at pH 4·5 were studied spectrophotometrically. It is established that Ga, Bi, Pb and Ag form stable complexes with extinction maxima at 255, 263 to 265, 240 to 241, and 300 mμ, respectively. The extinction curves of the other complexes do not show maxima. A spectrophotometric method is evolved for the determination of Bi in the presence of a 500-fold amount of Pb. To the soln. at pH 4 to 6 containing 0·5 to 7 μg of Bi per ml add 40 to 60 ml of 0·0001 *M* **I**, mix, dilute to 100 ml and measure the extinction at 263 to 265 mμ, with water as the comparison soln. Beer's law is obeyed for 0·5 to 7 μg of Bi per ml.
C. D. KOPKIN

2510. **Methods of concentrating traces of metals by co-precipitation. I.** V. T. Chuiko. *Zhur. Neorg. Khim.*, 1957, **2** (3), 685–695; *Ref. Zhur., Khim.*, 1957, Abstr. No. 69,089.—Study has been made of the concentration of Ni, Cd and Co by the pptn. of a substance acting as a collector with excess of a reagent (first method) and the concentration of Cu by pptn. of part of the macro component (second method). The co-pptn. of Ni, Cd and Co was carried out with the hydroxides of Mg, Cd, Fe and Bi, both by formation in the soln. and by addition as such. After 24 hr. the ppt. was separated from the soln. and the quantity of the metal to be concentrated was determined in the soln. and in the ppt. Nickel was determined colorimetrically, and Cd and Co by means of the radioactive isotopes ^{115}Cd and ^{60}Co. In concentrating Ni, Cd and Co (from soln. containing 5 μg of Ni or Cd per litre and 0·01 μg of Co per litre) by the first method, quant. co-pptn. (>90%) was achieved when the pH of the soln. exceeded the pH value for the pptn. of the hydroxides of the metals to be concentrated, whether or not the solubility product of the hydroxides had been reached. The co-pptn. of Cu

was carried out by the second method by means of the hydroxides of Zn and Cd. The quantity of Cu in the ppt. and soln. was determined colorimetrically. Quant. co-pptn. of Cu with a ppt. of a basic salt of the macro component was achieved only when a definite fraction of the macro component was pptd., which fraction must be established experimentally in each case. C. D. KOPKIN

2511. **Selective chelometric titrations of metal ions with triethylenetetramine.** C. N. Reilley and M. V. Sheldon (Dept. of Chem., Univ. of North Carolina, Chapel Hill, U.S.A.). *Chemist Analyst*, 1957, **46** (3), 59–62.—Triethylenetetramine (**I**) forms stable, soluble 1:1 complexes with Cu, Zn, Cd and Hg and can be used for titrations with metal-sensitive indicators. Potentiometric titration of Cu with a mercury electrode is used when the deep blue of the Cu - **I** complex obscures the indicator end-point, namely at concn. of Cu $> 0{\cdot}05$ m*M*. For Cd and Hg titrations, the end-point is detected by the Zn - zincon system. Eriochrome black T is satisfactory for Cd if alkaline and rare earths are absent. Details of preparations of reagents are given. *Cu and Zn*—For concn. $< 0{\cdot}05$ m*M* of Cu, add ammoniacal buffer, murexide indicator, and aq. NH_3 to pH 9·5. Titrate to a pink colour with **I**. For Zn proceed similarly, with zincon as indicator, titrating to a pure yellow. *Cd and Hg*—To 50 ml of soln. containing a small amount of Zn add 1 ml of ammoniacal buffer, aq. NH_3 to give a pH of 9·5 and some zincon. Titrate to a pure yellow with **I** and add the Cd or Hg sample. Zinc is displaced from the complex and recombines with zincon, giving a blue colour. Titrate with **I** to a pure yellow. The titration of Hg is conducted with triethanolamine buffer at pH 7·5 to 8 to keep Hg in soln. Results are tabulated. Two-component mixtures can be determined by using two complexing agents, *e.g.*, EDTA and **I**. Thus, for Ca - Zn, the total metal content is determined by titration with EDTA, and Zn alone by titration with **I**. R. L. MORTLOCK

2512. **High-frequency titration [of metals] with sodium hydrogen sulphide.** Tadashi Kikuchi, Akira Yamada and Kunio Nakano (Gov. Chem. Ind. Res. Inst., Yoyogi P.O., Tokyo). *Japan Analyst*, 1957, **6** (10), 658–661.—The high-frequency titration of Zn, Cu and Cd with standard NaHS soln. was studied with a TPTG-type oscillator (Jensen *et al.*, *Anal. Chem.*, 1951, **23**, 1329). The conductivity of the soln. first increases ($ZnSO_4 + NaHS = ZnS + NaHSO_4$) and then decreases ($NaHSO_4 + NaHS = H_2S + Na_2SO_4$; H_2S is negligibly dissociated), the max. point indicating the end-point. The optimum acid concn. is 0·05 *N* for Zn and Cd and $\simeq 1$ *N* for Cu. No interference results from NH_4^+ used for the adjustment of the acid concn. The vol. of 10% NaHS increases linearly with the concn. of the metal ion for < 1 g of Zn and Cd, and $< 0{\cdot}6$ g of Cu per 60 ml. The NaHS soln. is standardised by the titration of pure Zn. Copper and Zn are titrated successively in 0·05 and 1 *N* H_2SO_4 soln. This method is applicable to the rapid determination of Zn in electrolytic soln. for refining. The results compare favourably with those by the titration with $K_4Fe(CN)_6$. K. SAITO

2513. **Qualitative inorganic analysis by paper chromatography: separation of common cations.** E. Pfeil, A. Friedrich and T. Wachsmann (Chem. Inst. der Univ. Marburg). *Z. anal. Chem.*, 1957, **158** (6), 429–434.—Use Binzer 202 paper for all separations. For metals of the H_2S group, develop with butanol - 3 *N* HCl; identify Ag, Te, Mo, Se and Hg with H_2S; Cu, Pb, Sb, Bi, As and Hg with aq. KI; Ge and Sn with quercetin soln.; Cd with aq. $(NH_4)_2S$. For the Pt-group metals, develop with butanol - 3 *N* HCl; identify Os and Ru with thiourea; Pt with aq. KI; Pd with aq. H_2S; Ir with aq. Br; Rh with a soln. of $SnCl_2$ in conc. HCl. For metals of the $(NH_4)_2S$ group, develop with acetic acid - pyridine - conc. HCl (80:6:20); identify Fe and Zn with a mixture of a saturated soln. of diethylaniline in 4% oxalic acid and 4% $K_3Fe(CN)_6$ soln.; Mn with ammoniacal H_2O_2; Co and Ni with aq. $(NH_4)_2S$; Al with an ethanolic soln. of morin; Cr with aq. NH_3; U, W, V and Ti with quercetin soln. For metals of the ammonium carbonate group, develop with methanol - acetic acid (98:2); identify Be with morin soln.; Ra by its radioactivity; Mg, Ca, Sr and Ba with ethanolic bromocresol green. For Li, Na and K, develop with methanol - acetic acid (98:2) and identify with bromocresol green. Limits of sensitivity and R_F values are given. (*Cf.* Pfeil *et al.*, *Anal. Abstr.*, 1955, **2**, 2938.) A. R. ROGERS

2514. **High-voltage paper electrophoresis of some inorganic anions.** D. Gross (Tate and Lyle Res. Lab., Keston, Kent, England). *Chem. & Ind.*, 1957, (49), 1597.—Many anions can be easily and rapidly separated by electrophoresis for 20 min. on Whatman No. 3 MM paper, with 0·1 *M* aq. ammonium carbonate, 100 V and 13 mA per cm, and cooling water at 12°. Separation of Br^- from Cl^- takes 35 min. with strip extension (*cf.* Gross, *Nature*, 1957, **180**, 596). The spots are revealed with a soln. of 0·05% bromocresol purple in 90% ethanol, and are confirmed by specific reagents. The repeatability is within 5%; the temp. of the strip varies by $< 2°$. Rates of migration for 20 anions relative to $Cl^- = 1{\cdot}00$ are listed, the value for Cl^- being taken as $34{\cdot}6 \times 10^{-5}$ cm^2 V^{-1} sec.$^{-1}$. W. J. BAKER

2515. **Analysis of lung dusts. II. Separation and determination of iron, aluminium, titanium, calcium, magnesium and phosphate in dust samples.** J. Fitzek and H. Stegemann. *Beitr. Silikose-Forsch.*, 1957, No. 47, 41–48.—Dry lung dust (75 to 300 mg, according to the carbon content) is ignited at 700° for 3 hr., first in air and finally in O. The residue is heated to fuming for 10 min. on a water bath with 10 to 15 ml of 40% HF, and then with 6 *N* HCl (3 × 5 ml). The residue is dissolved in 5 ml of 6 *N* HCl and the soln. is passed through a column (20 cm × 20 cm) of Lewatit KSN at the rate of 4 ml per min., and the column is then eluted with 150 ml of 0·15 *N* HCl. The eluate is diluted to 250 ml, and an aliquot is used for the determination of P by the vanadate - molybdate method (*cf.* Gericke and Kurmies, *Brit. Abstr. C*, 1953, 59). The cations retained on the Lewatit column are eluted with 200 ml of 4 *N* HCl, the vol. of the eluate is reduced to 10 ml, and Fe, Al and Ti are pptd. by boiling and addition of 2 *N* aq. NH_3. The ppt. is separated by centrifuging, and the supernatant liquid is evaporated to remove NH_3, then dissolved in water or dil. HCl, and titrated with EDTA (disodium salt) to give Ca and Mg. The ppt. containing Fe, Al and Ti is dissolved in 10 ml of 8 *N* HCl and the soln. is passed through a column of Amberlite IRA-400, previously washed with 8 *N* HCl. An aliquot of the eluate, which contains Al and Ti, is used for

the colorimetric determination of Ti, after treatment with H_2O_2, and for the determination of Al by the 8-hydroxyquinoline method (*cf.* Berg, *Z. anal. Chem.*, 1930, **86**, 369). Iron is eluted from the Amberlite IRA-400 with 0·1 *N* HCl, and determined as the phenanthroline complex (*cf.* Bencze, *Z. anal. Chem.*, 1948, **128**, 179).

J. L. PROSSER

2516. **Method for weighing pure alkali metals accurately.** F. A. Lewis (Chem. Engng Dept., Imperial Coll., London, England). *Chem. & Ind.*, 1957, (46), 1504–1505.—The potassium (in a broken ampoule) is placed in the side-arm of the all-glass apparatus described, from which, after desorption of impurities by heating *in vacuo* and re-cooling, it is distilled and finally forced by gas pressure in a molten state into an ampoule formed by the lower part of a weighed glass tube. This ampoule (after being sealed) is weighed, as is also the upper part of the glass tube (after removal of trace amounts of potassium). The wt. of potassium is obtained by difference. Pure N or A is passed through the apparatus during the operations. W. J. BAKER

2517. **Further data on the determination of alkali hydroxides in the presence of alkali carbonates.** E. Bakács and L. Szekeres (Univ. for Agric. Sci., Budapest). *Magyar Kém. Foly.*, 1957, **63** (11), 325–326.—The effect of impurities on the method (*cf. Anal. Abstr.*, 1958, **5**, 1115) is examined. Acetate, Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, IO_3^-, SO_4^{2-}, CrO_4^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, NO_2^- and NO_3^- do not interfere; the method cannot be used in the presence of F^-, PO_4^{3-} and $B_4O_7^{2-}$. If NH_4NO_3 is present, the OH^- concn. as determined is somewhat low; other impurities, *e.g.*, Na_2SO_3, $NaNO_2$ and K_2CrO_4, improve the end-point. If the concn. of CO_3^{2-} is much higher than that of OH^-, the titration with $ZnCl_2$ near the end-point must be even slower than usual. A. G. PETO

2518. **Quantitative determination of lithium in the presence of sodium and potassium by the phosphate method.** P. S. Kindyakov and A. V. Khokhlova. *Trudy Moskov. Inst. Tonkoĭ Khim. Tekhnol.*, 1956, (6), 9–14; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,652.—The influence of pH, quantity of precipitant (Na_2HPO_4) and the presence of K and Na on the completeness of pptn. of Li_3PO_4 was studied. An improved method for the determination of Li as Li_3PO_4 is proposed. To 10 ml of the hot soln. add excess (30%) of Na_2HPO_4, cool, neutralise with 5% NaOH soln. to phenolphthalein and evaporate to dryness while maintaining the pH constant. To the residue add 10 ml of 2·5% aq. NH_3 and filter after 3 or 4 hr. Repeat this treatment on the filtrate, combine the residues and ignite at 800°. For a sample of 12 mg of Li_2SO_4 the error is ± 0·5%. The method is simple and does not require preliminary removal of Na and K.

C. D. KOPKIN

2519. **Rapid method for the determination of potassium in minerals.** I. G. Gurvich and E. I. Khanaev. *Izv. Akad. Nauk, SSSR, Ser. Geol.*, 1957, (4), 104–107; *Ref. Zhur., Khim.*, 1957, Abstr. No. 69,122.—A rapid method is evolved for the decomposition of minerals by fusion with $CaCl_2$. Grind the sample to a particle size of 0·25 to 0·15 mm, and to 0·2 g in a graphite crucible add $CaCl_2$ (1·2 g) and heat for 20 min. at 200°. Place the crucible in a quartz tube of length 400 mm, close the tube and place it in a cooling sleeve with running water which is in the centre of a H.F. generator inductor, and heat to between 1500° and 1700°. Extract the melt with water, filter, dilute and determine the K spectrographically. The mean relative error in determining K in muscovite is < 0·97%. C. D. KOPKIN

2520. **Rapid radiometric determination of potassium with a Geiger-Müller counter.** H. Dresia and R. Beckmann (Inst. für Chem. Technol., Tech. Hochschule, Aachen, Germany). *Z. anal. Chem.*, 1957, **159** (1), 1–12.—Potassium is determined radiometrically by measurement of the β-activity of ^{40}K in soln. For a given accuracy, the time of the analysis is reduced by employing two or three similar counters connected in parallel, coincident countings having no effect on the accuracy. Up to 3% of suspended matter causes no interference, but asymmetric positioning of the counter in the soln. leads to errors due to the γ-activity. Continuous recording of K in soln. can be made by connection to a suitable integrating measuring device. J. H. WATON

2521. **The solubility of some potassium, rubidium and caesium compounds.** Kyoji Toei (Chem. Dept., Fac. of Sci., Okayama Univ., Tsushima). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (9), 1379–1385.—The solubility in water of the potassium, rubidium and caesium salts of "hexyl," "dihexyl," "thiohexyl," tetranitroacridone (*Anal. Abstr.*, 1955, **2**, 3290; 1956, **3**, 2409), 2:4-dinitronaphthosultam, tetranitrophenothiazine (*Anal. Abstr.*, 1957, **4**, 374, 1438), benzenesulphonyl-2:4-dinitronaphthylamine and picric acid was studied at various temp. There is a linear relationship between the log of the molar fraction of the saturated soln. and the reciprocal of the absolute temp., the gradient being almost equal for these metal ions. In general, the solubility decreases in the sequence K, Rb, Cs. The solubility is also discussed stoicheiometrically. K. SAITO

2522. **Triethylenetetramine (trien) as an analytical reagent. II. Photometric titrations of copper in the presence of other metals.** H. Flaschka and A. Soliman (Nat. Res. Centre, Dokki, Cairo, Egypt). *Z. anal. Chem.*, 1957, **159** (1), 30–35.—Photometric titrations with triethylenetetramine, in the form of its sulphate, are highly selective (*cf. Anal. Abstr.*, 1958, **5**, 2115). Of the common metals tested, only Hg, Ni, Co, Al and Cr interfere, and the sulphate form of the reagent should not be used if Sr and Ba are present. The interference of Hg is easily overcome by the addition of KBr. If Ni and Co are present, the titration is carried out at pH 5, the addition of tartrate being necessary for Ni and optional for Co. In the presence of Al, the titration is performed at pH 5, or 10 in the presence of citrate. Interference due to Cr is easily avoided by oxidation to Cr^{VI}. The procedure enables Cu to be determined titrimetrically in the presence of oxidising agents. The method has been applied to the determination of Cu in aluminium alloys. J. H. WATON

2523. **Complexometric determination of copper and manganese in the presence of each other.** G. Martens and K. Schwartz (Chemiewerk Greiz, Dölau, Germany). *Z. anal. Chem.*, 1957, **159** (1), 22–25.—The sum of Mn and Cu is determined at pH 6 to 6·5 by displacement of Zn from excess of its EDTA complex. Then excess of 0·01 *M* EDTA (disodium salt) is added to complex the Zn, and the

excess is determined with 0·01 *M* $ZnSO_4$ and Eriochrome black T at the b.p. of the soln. Iron interferes if its concn. is > 3 mg per litre. Manganese alone is determined by Flaschka's method (*Chemist Analyst*, 1953, **42**, 56) in the presence of Na K tartrate, NH_4Cl - aq. NH_3 buffer, ascorbic acid and KCN, by titration with 0·01 *M* EDTA (disodium salt) at 70° to 80° until the Eriochrome black T indicator changes from red to blue - green. The method is suitable for the determination of Cu and Mn in catalysts, raw materials and intermediate products. J. H. WATON

2524. **A spectrochemical solution method for the determination of copper, cobalt and iron in copper and cobalt concentrates.** G. L. Mason and Z. de Beer (Rhoanglo Mine Services Ltd., Res. and Development Div., Kitwe, N. Rhodesia). *Analyst*, 1958, **83**, 129–135.—The sample (0·5 g) is gently heated with conc. HNO_3 and Br, then with conc. HCl and finally with $HClO_4$ and is then evaporated to a pasty mass. The residue is dissolved in HCl and diluted to a known vol. For the determination of Cu and Fe (3 to 40%) and Co (1 to 6%), 5 ml of the sample soln. is mixed with 1 ml of a standard nickel soln. For a low content of Co (0·15 to 1%), a 10-ml portion of the sample soln. is used. The preparation of synthetic standard soln. and the procedure for recording the spectrograms are described. Spectrographic and photographic data are quoted. Standard graphs are constructed for the standard soln. by plotting the log. of the intensity ratio against the log. of the concn. of metal. A. O. JONES

2525. **Spectrophotometric determination of copper in non-ferrous metals with neocuproin.** Yoshihiro Ishihara and Yasuro Taguchi (Mining Res. Inst., Mitsubishi Mining Co., Oomiya, Saitama Prefecture). *Japan Analyst*, 1957, **6**, (9), 588–589.—The colorimetric (457 mμ) determination of Cu (1 to 10 μg) with neocuproin (**I**) (Smith *et al.*, *Anal. Chem.*, 1952, **24**, 371) was applied to the analysis of metallic zinc, cadmium, lead, bismuth and tin. Interference results from > 25 times the weight of Ag and Be (relative to Cu), but not from < 1 mg of most other metals, nor from < 2 g of Zn, Cd, Pb or Bi. Zinc, cadmium or bismuth metal is dissolved in HNO_3 (1 + 1, 15 to 20 ml) and diluted. A portion is treated with hydroxylamine hydrochloride (10%, 2 ml; for Bi 30 ml), Na citrate (30%, 2 ml), and aq. NH_3 soln. to give a pH of 4·5. The product is treated with **I** by the usual method (*loc. cit.*). For lead metal, Na acetate (30%, 5 ml) is used in place of Na citrate. Tin metal (1 g) is treated with HBr (48%, 10 ml) and saturated aq. Br soln. (2 ml), dissolved in HNO_3 (1 + 1, 10 ml), and treated similarly. K. SAITO

2526. **Analysis of nickel alloys for oxide cathodes. IV. Determination of copper.** K. Riedel (Wernerwerk für Bauelemente, Siemens und Halske A.-G., München, Germany). *Z. anal. Chem.*, 1957, **159** (1), 25–29.—A colorimetric procedure is described for the determination of Cu in the presence of a 10,000-fold excess of Ni. After dissolution of the sample in HNO_3, the pH is adjusted to 3·5, whereupon the Cu, together with an equiv. amount of Ni, is extracted by shaking for ≃ 0·5 min. with a CCl_4 soln. of Cd diethyldithiocarbamate (**I**). Copper, Ni and Cd are then transferred back to an aq. phase by shaking with aq. $HgCl_2$ soln. After complexing the Ni with EDTA (disodium salt), excess of which is removed by the addition of $MgSO_4$ soln., the Cu is re-extracted with the CCl_4 soln. of **I**. The colour of the organic layer is then due solely to Cu diethyldithiocarbamate, the extinction of which is measured. Small amounts of Ag and Hg do not interfere. The analysis can be completed in ≃ 30 min. J. H. WATON

2527. **Determination of copper and zinc in alloys [brass and bronze] by amperometric titration with a rotating platinum micro-electrode.** V. A. Khadeev and A. K. Zhdanov (V. I. Lenin Central Asiatic State Univ.). *Zavod. Lab.*, 1957, **23** (11), 1290–1291.—Titration of Cu is carried out with KSCN soln. at 0·3 V in the presence of ascorbic acid, which reduces Cu^{2+} and also small amounts of HNO_3 that may be left after dissolution of the alloy. In the same soln., without removal of the pptd. CuSCN, titration of Zn is carried out with $KHg(SCN)_4$ soln. at 0·08 V after the rotating platinum electrode has been given a period of anodic polarisation from another source of e.m.f. With brass and bronze the error is ± 1% of the content of Cu or Zn. No interference in the determination of Cu is caused by the presence of Mg, Fe, Mn, Ni, Co, Zn, Cr, Al, Cd and Pb, but Bi and Cl^- interfere. G. S. SMITH

2528. **Quality control of copper cathodes by an acidimetric nitrilotriacetate titration.** J. Kinnunen and B. Merikanto (Outokumpo Oy, Metalworks, Pori, Finland). *Chemist Analyst*, 1957, **46** (3), 62.—The method is used for determining free H_2SO_4 and combined SO_4^{2-} on the surface of copper cathodes. The surface is washed with H_2O, and H_2SO_4 in the washings is titrated with 0·1 *N* NaOH to methyl red. Sulphate combined with Cu or Ni is determined by adding 1 ml of 0·1 *N* Na nitrilotriacetate (**I**) and titrating with 0·1 *N* NaOH, repeating till the addition of **I** does not change the indicator colour. R. L. MORTLOCK

2529. **The micro-heterometric determination of silver with *p*-dimethylaminobenzylidenerhodanine. Direct determination of traces of silver in alloys and solutions.** M. Bobtelsky and J. Eisenstadter (Hebrew Univ., Jerusalem). *Anal. Chim. Acta*, 1957, **17** (5), 503–511 (in English).—Silver present to the extent of 0·02 to 0·04% in thorium, uranium, mercury, lead, bismuth, zinc or copper, or 0·1 to 0·2% in other metals, can be determined within 2% by titration in ammoniacal soln. with ethanolic *p*-dimethylaminobenzylidenerhodanine. The end-point is indicated by the extinction plot of the suspended ppt. at 525 mμ becoming horizontal. Interference by foreign metals is prevented by the addition of complexing agents. For most mono- or bi-valent metals, Na citrate is used and Na tartrate is used for most polyvalent metals. EDTA is required in the presence of Hg or Tl. A titration takes ≃ 5 min. G. BURGER

2530. **The determination of silver, palladium(II) and copper(I) by means of radiometric titration, with iodine-131 as indicator.** G. Tölgyessy and P. Schiller (Slovakian Tech. Univ., Bratislava, Czechoslovakia). *Magyar Kém. Foly.*, 1957, **63** (10), 269–271.—The soln., contained in a beaker provided with a stirrer, is titrated with KI labelled with ^{131}I. A glass tube, protected by a glass-filter, reaches into the liquid; to its other end, a syringe is attached, and its middle portion forms a spiral, which surrounds a Geiger counter. When the ppt. in the liquid has settled, the activity of the soln. is determined by drawing the liquid into the glass spiral. If the curve of activity against KI added

is plotted, the point of deflection gives the equivalence point. It is more convenient to calculate the value by Langer's method (*Anal. Chem.*, 1950, **22**, 1288) from the activity of the soln. after adding two different amounts of labelled KI soln. The accuracy is greatly improved by correcting for the increase in the vol. of the soln. to be determined during titration. A. G. PETO

2531. **Present state of the analytical chemistry of beryllium.** V. G. Goryushina. *Zavod. Lab.*, 1957, **23** (11), 1300–1307.—A review with 86 references is presented. G. S. SMITH

2532. **Spectrographic analysis of beryllium.** P. M. Polyakov, A. K. Rusanov and I. M. Blokh. *Zavod. Lab.*, 1957, **23** (11), 1320–1323.—Conditions for the determination of Al, Ba, V, Bi, W, Fe, Cd, K, Ca, Co, Si, Li, Mn, Mg, Cu, Mo, As, Na, Ni, Nb, Sn, Pb, Ag, Sb, Ta, Ti, Cr, Zn and B in beryllium are described. The sample is first oxidised in a current of O. G. S. SMITH

2533. **Estimation of beryllium. II. New rapid gravimetric method for its estimation in beryl.** Apurba Kumar Sen Gupta (Univ. Coll. of Science, Calcutta). *J. Indian Chem. Soc.*, 1957, **34** (10), 725–727.—The sample is fused with $NaBF_4$, the melt is leached with hot water, and the extract is adjusted to a pH of 7·2 to 7·4 by the addition of $NaHCO_3$, boiled, and filtered. The Be in the filtrate is pptd. as $BaBeF_4$. The advantages of the method over others are discussed. I. JONES

2534. **Determination of beryllium in ores by means of photoneutrons.** B. S. Aldarkin, G. V. Gorshkov, A. G. Grammakov, V. S. Zhadin and A. G. Kolchina. *Trudy Radiev. Inst., Akad. Nauk*, SSSR, 1957, **5** (2), 89–93; *Ref. Zhur., Khim.*, 1957, Abstr. No. 66,388.—The method is based on the use of the nuclear photo-effect on Be and on the artificial radioactivity caused by neutrons. By irradiation with γ-rays of the energy appropriate to the compound containing Be, neutron emission is caused, the intensity of which within satisfactorily wide limits in known conditions is proportional to the concn. of Be. To increase the accuracy of the results, it is necessary that the densities of the substance and of the standard should not greatly differ and that the concn. of Be in the sample and standard should not differ by more than 5 or 10 times; also the same wt. of sample and standard should be taken, while using the same area of the irradiated layer. C. D. KOPKIN

2535. **Volumetric determination of magnesium in titanium.** M. J. Miles, W. J. Mesimer and M. Atkin (Titanium Metals Corp., Henderson, Nev., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 361–363.—More than 0·02% of Mg in titanium sponge, alloy or leach liquor can be determined by titration at pH 10 with standard EDTA soln., and Eriochrome black T mixed with methyl red as indicator. Titanium and Fe are removed initially by separation with ammonium acetate, whilst the effect of Mn on the indicator is eliminated by addition of 5% Na_2S soln. (5 ml) to the filtrate (100 ml) and boiling for $\simeq$ 10 min. Reducing or strong oxidising agents, PO_4^{3-} and F^- should be absent. The error is $< 1\%$ unless the content of Mg is $< \simeq 0{\cdot}1\%$, when the error can rise to 5%. W. J. BAKER

2536. **Separation of small amounts of magnesium from iron with ammonium sulphide.** H. Gamsjäger and R. Reichert (Montan. Hochschule, Leoben, Austria). *Z. anal. Chem.*, 1957, **158** (5), 356–358.—Use is made of $MgSO_4$ labelled with ^{27}Mg to show that no loss of Mg by co-pptn. with FeS occurs in the method for the determination of Mg in iron described previously (*cf.* Reichert, *Anal. Abstr.*, 1956, **3**, 2737). A. R. ROGERS

2537. **Complexometric determination of calcium and magnesium in iron ore with the use of cationites.** O. V. Datsenko (M. I. Arsenichev Dnieprodzerzhinsk Metallurgical Inst.). *Zavod. Lab.*, 1957, **23** (11), 1296–1298.—The sample (0·5 g) is dissolved in 15 ml of conc. HCl, the soln. is evaporated to a syrup, which is dissolved in 30 ml of hot dil. HCl (1:4), and the insoluble matter is filtered off and washed with water containing acid. The filtrate is evaporated to between 2 and 3 ml, the soln. is diluted to 30 ml with water, 20 ml of 20% citric acid soln. is added, and aq. NH_3 is added dropwise until the odour of NH_3 persists. The liquid is passed at a rate of 5 ml per min. through a column of SBS (NH_4^+ form) and the column is washed three or four times with water, the filtrate and washings containing Fe and Al being rejected. To obtain the Ca and Mg, the column is washed with 100 ml of dil. HCl, followed by water. The Ca and Mg are determined in the eluate by EDTA titration. G. S. SMITH

2538. **The effect of aluminium on the emission of calcium in the flame.** C. T. J. Alkemade and M. E. J. Jeuken (Fysisch Lab., Rijks-Univ., Utrecht, Holland). *Z. anal. Chem.*, 1957, **158** (6), 401–409.—The quenching effect of $Al(NO_3)_3$ in the flame-photometric determination of Ca is attributed to the formation of a Ca - Al - O complex in the aerosol particles. If the Al is present as the chloride, complex formation apparently occurs in the gas phase. Applications to the analysis of calcium and aluminium soln. are discussed. A. R. ROGERS

2539. **Flame-photometric determination of calcium in phosphate, carbonate and silicate rocks.** H. Kramer (U.S. Geol. Survey, Washington, D.C., U.S.A.). *Anal. Chim. Acta*, 1957, **17** (5), 521–525 (in English).—Interferences can be overcome by the addition of the interfering elements in such amounts that further addition causes no further increase or decrease in the emission due to Ca. These elements are added in the form of a soln. containing 400 p.p.m. of Al, 250 p.p.m. of P, 900 p.p.m. of Mg, 50 p.p.m. of Fe, 80 p.p.m. of Na, 30 p.p.m. of K and 6 ml of HNO_3 in 100 ml of soln.; 20 ml of this soln. is added to a soln. of 1 g of rock. The soln. is aspirated into the oxy-hydrogen flame and the emission is measured at 554 mμ with a blue-sensitive phototube. Results obtained are within $\pm$ 2% of the CaO content. The lower limit of sensitivity is 0·01%. G. BURGER

2540. **Determination of calcium and silver in photographic materials via EDTA titrations.** G. Sjöstedt and L. Gringras (AB Ceaverken, Strängnäs, Sweden). *Chemist Analyst*, 1957, **46** (3), 58–59.—Variable amounts of Ca retained by the gelatin in which the silver halide ions are embedded interfere in the determination of Ag based on interaction with potassium nickel tetracyanide and complexometric titration of displaced Ni. The Ca can be easily removed by prior washing of the gelatin

layer with dil. HCl (100 ml of water to 1 ml of *M* HCl), and determined in the washings by the use of EDTA, with murexide as indicator. The washed gelatin is shaken with ammoniacal NH_4Cl buffer soln., potassium nickel tetracyanide soln. and aq. NH_3 to ensure dissolution of the silver halide, and the displaced nickel is titrated with EDTA, with murexide as indicator. Results tabulated are in good agreement with those from the more tedious Volhard method. R. L. MORTLOCK

2541. **Gravimetric determination of barium in zirconium metal and in certain zirconium salts.** L. Silverman and K. Trego (N. Amer. Aviation, Inc., Canoga Park, Calif., U.S.A.). *Anal. Chim. Acta*, 1957, **17** (3), 280–285 (in English). *Cf. U.S. Atomic Energy Comm.*, Rep. NAA-SR-1720, 1957, 17 pp. (*Anal. Abstr.*, 1958, **5**, 1131.)

2542. **The development and evaluation of radiochemical separation procedures for barium, calcium, strontium, silver and indium.** D. N. Sunderman (Univ. of Michigan, Ann Arbor, U.S.A.). *Dissert. Abstr.*, 1957, **17** (6), 1207–1208.—Optimum conditions of yield and decontamination have been determined for radiochemical separations of Ba, Ca, Sr, Ag and In in tracer soln. Yields and decontamination factors (*D*) are given for separations of Ba^{2+}, Ca^{2+} and Sr^{2+} by pptn. as NO_3^-, Cl^- or CrO_4^{2-}. The pptn. of hydrous oxides of Fe^{3+} and La^{3+} as scavengers is described, and their action and efficiency is evaluated. Higher decontamination can be attained by scavenging in the presence of carrier amounts of the decontaminant. A quant. procedure, comprising isotopic exchange with a AgCl surface, is described for the separation and determination of ^{107}Ag in a radiochemical soln., fission-product mixtures or bombardment samples. The method, which is valid in the presence of high concn. of inorganic salts and organic solvents, is highly specific, with $D = 10^3$ to 10^7 for 18 radioactive elements. Values of *D* in the separation of ^{107}Ag by pptn. as AgCl or with benzotriazole in ammoniacal EDTA soln. are 40 to 200, whilst by electrolysis they are 100 to 500. Separation of In by sulphide pptn. is non-specific as a decontamination step, and anion exchange of In in HCl soln. becomes non-specific when the rate of flow is high. In the ether extraction of $InBr_3$, values of $D = 10^4$ are usually attainable for dissimilar elements under strictly standardised conditions. W. J. BAKER

2543. **Determination of radium aerosols in the presence of other α-active aerosols.** O. S. Andreeva and E. E. Kovalev. *Gigiena i Sanit.*, 1957, (5), 27–30; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,662.—To determine radium aerosols in the presence of other α-active aerosols, the emanation method is used. This consists in drawing 1000 to 2000 litres of the air through a filter, dissolving the Ra in 15% HNO_3 and determining the content of Ra by measuring the Rn collected after 3 days and measuring the ionisation current with an electrometer. The accuracy of the method is within ± 30%. C. D. KOPKIN

2544. **Spectrographic analysis of high-purity zinc by means of vacuum sublimation.** D. M. Shvarts and L. N. Kaporskiĭ (Gipronikel' Inst.). *Zavod. Lab.*, 1957, **23** (11), 1309–1313.—Most of the Zn is distilled off in a vacuum and the residue is subjected to spectrographic analysis. Impurity contents of $\simeq 10^{-5}$ to 10^{-3} % can be determined with an error of $\simeq$ 20%. G. S. SMITH

2545. **Determination of zinc and separation from ashed biological material.** J. A. Stewart and J. C. Bartlet (Dept. of Nat. Health and Welfare, Ottawa, Canada). *Anal. Chem.*, 1958, **30** (3), 404–409.—4-Chlororesorcinol, 4-bromoresorcinol and resorcinol were compared as colorimetric reagents for Zn; 4-chlororesorcinol gave the best results, Beer's law being obeyed over the range 0·1 to 5 p.p.m. of Zn at 640 mμ. The cation interferences are very similar to those reported for resorcinol, but the Zn is separated from these in the ash of biological material by extraction from aq. soln. into $CHCl_3$ as the diethyldithiocarbamate. The Zn is back-extracted into aq. 0·16 *M* HCl and is determined colorimetrically. The average recoveries at the 15-μg and 50-μg levels are 100 and 97%, and the coefficients of variation are ± 1·4 and ± 2·2%, respectively. The mean recovery of Zn added to ash from agar is 95·4%. When zincon was used as a colorimetric reagent for Zn, in conjunction with the diethyldithiocarbamate extraction, the average recovery was 97%. G. P. COOK

2546. **EDTA titration of zinc in brass and bronze, and of cobalt in the presence of copper.** E. Körös and Z. Remport-Horvath (L. Eötvös Univ., Budapest, Hungary). *Chemist Analyst*, 1957, **46** (4), 91–92.—Zinc is determined by EDTA titration at pH 4·5 to 6 with xylenol orange as indicator. Interference due to Cu can be overcome by reduction with ascorbic acid to Cu^I, and pptn. as iodide or thiocyanate. Successive determination of Cu and Zn is possible by addition of iodide and titration of the liberated iodine, followed by EDTA titration of the Zn. The Cu and Co in ferromagnetic alloys may be determined by iodimetric titration and EDTA titration (at pH 5 to 6 with xylenol orange), respectively. Full analytical details are given. G. S. ROBERTS

2547. **Chelatometric determination of zinc, cadmium and lead ions with Variamine blue as redox indicator.** L. Erdey and L. Pólos (Tech. Hochschule, Budapest). *Anal. Chim. Acta*, 1957, **17** (5), 458–462 (in German).—Zinc, Cd and Pb can be determined by direct titration with EDTA in the presence of Variamine blue and a redox system comprising one or two drops of a mixture of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ soln. The soln. must be buffered at pH 5. The end-point is indicated by a change from violet to colourless. The mean values of triplicates for 11 determinations show a range of error of − 1·6% to + 0·5%. Alkali and alkaline-earth metals or Mg^{2+} do not interfere. Magnesium can be determined in the same soln. after addition of aq. NH_3 - NH_4Cl buffer soln., with Eriochrome black T as indicator. The determination of Pb separated as sulphate can be shortened by conversion into the carbonate, which can be dissolved in acetic acid, neutralised and titrated as described above. G. BURGER

2548. **New rapid gravimetric method for the determination of cadmium.** E. Poper, L. Popa, V. Junie and L. Roman (Lab. de Chim. Anal., Fac. de Farm., Cluj, Romania). *Rev. Chim., Bucharest*, 1957, **8** (11), 714–716.—*Procedure*—To 0·01 to 0·15 g of the cadmium salt dissolved in 10 to 15 ml of water is added an equal quantity of ethanol, and the soln. is heated on a water bath. By means of a pipette a 0·5% ethanolic soln. of 1-phenylthiocarbamoyl-2-thiocarbamoylhydrazine is added dropwise, with continual stirring. The reaction mixture is set aside on the water bath for

approx. 15 min., then the white amorphous ppt. is filtered off and washed with hot 50% ethanol, 2 to 5 ml of absolute ethanol, and finally 3 to 5 ml of diethyl ether. It is then dried at 105° to 110° for 20 to 30 min. An accuracy of + 0·3 to − 0·2% is claimed for the determination, which takes 2 hr.
H. SHER

2549. **Use of co-precipitation for obtaining analytical concentrates of cadmium, lead, bismuth and zinc in the analysis of alloys [molybdenum and tungsten with nickel].** A. K. Babko and P. V. Marchenko (Inst. of Gen. and Inorg. Chem., Acad. Sci, USSR). *Zavod. Lab.*, 1957, **23** (11), 1278–1283.—The most favourable pH for the pptn. as sulphides of Cd, Bi, Pb and Zn in the presence of Mo and Ni is between 3 and 4, but the separation from Ni is unsatisfactory since H_2S reacts with Ni more quickly than with the other metals. Decrease of pH leads to pptn. of Mo. With W - Ni alloys a satisfactory separation of Cd, Bi and Pb can be obtained at pH 2 to 3 in the presence of tartaric acid (5 g for each 1 g of alloy) if $HgCl_2$ is added to give HgS as collector. In ammoniacal medium (pH ≮ 10) the use of H_2S in the presence of pyridine or thioacetamide gives complete separation of Cd, Bi and Pb from soln. of Mo - Ni and W - Ni alloys, with the formation of only small amounts of NiS if the amount of H_2S is limited. With the thioacetamide method, 1 to 3 g of the Mo - Ni alloy is dissolved in 20 ml of a mixture of HNO_3 and HCl (1:1), or 1 to 3 g of W - Ni alloy is dissolved in dil. HNO_3 and 5 g of H_3PO_4 per 1 g of alloy. Oxides of N are boiled off, the diluted soln. is treated with aq. NH_3 until a blue colour appears, heated, and thioacetamide (0·1 g) or pyridine (10 ml) is added, followed by 20 ml of saturated H_2S water. The closed flask is set aside for 1 hr. for the ppt. to coagulate. After filtration the ppt. is washed with hot dil. aq. NH_3 and ignited.
G. S. SMITH

2550. **Synthesis of derivatives of dithizone and their application to analytical chemistry. II. oo′-Dimethyldithizone and its application to the determination of mercury and copper.** Shinsuke Takei (Dept. of Applied Chem., Fac. of Engng, Tohoku Univ., Sakurakoji, Sendai). *Japan Analyst*, 1957, **6** (10), 630–636.—*oo′*-Dimethyldithizone (**I**), synthesised by Preund's method (*Ber.*, 1891, **24**, 4178), has max. absorption at 460 and 628 mμ. The max. absorption of its complexes with Zn, Cd, Pb, Cu, Hg, Ag and Bi is at a wavelength shorter than that of the corresponding dithizone complex. Mercury (≯ 30 μg) is extracted (pH 2 to 7) with **I** into CCl_4 in the presence of < 20 mg of Pb and < 200 mg of Zn, Cd, Co and Ni. The presence of Cl^- (< 5 *M*) does not cause interference at pH > 3·5; Cu (< 100-fold) is masked with EDTA. Copper (< 10 μg) is extracted at pH 2·0 to 4·5 by shaking with **I** for 5 min.; there is no interference from < 5 mg of Bi or < 10 mg of Pb. The separation of Hg and Cu was unsuccessful. Thiocyanate is the best masking agent for Ag.
K. SAITO

2551. **Electrophoresis of the halogen complexes of mercury(II), bismuth(III), cadmium(II), lead(II) and copper(II). I. Chloro complexes in hydrochloric acid.** Z. Pučar (Inst. "Ruder Bošković", Zagreb, Yugoslavia). *Anal. Chim. Acta*, 1957, **17** (5), 476–484 (in German).—A liquid-cooled apparatus is described with which electrophoresis can be conducted on paper strips (700 mm × 15 mm) at voltages up to 3 kV and currents up to 250 mA. The voltage is adjusted according to the resistance of the saturated strip to give a power consumption of 71 to 73 W. With this apparatus the mobilities of Hg^{II}, Bi^{III}, Pb^{II} and Cu^{II} have been determined to within ± 5% on paper saturated with HCl of concn. from 0·1 *N* to 6 *N*. Complete separation of these metals can be achieved. The zones are identified by treatment with H_2S followed by NH_3. Correction of the mobility values for the effect of paper porosity is discussed.

II. Dependence of the mobilities on the concentration of the metal ions. Z. Pučar. *Ibid.*, 1957, **17** (5), 485–488.—The mobilities of these complexes on paper saturated with HCl depend not only on the concn. of the HCl, but also on the concn. and vol. of the salt soln. applied. Cationic mobility increases and anionic mobility decreases with increasing amount of salt applied. This effect is negligible when the concn. of HCl soln. on the paper exceeds 1 *N*.
G. BURGER

2552. **Spectrographic semi-quantitative determination of boron in ores and minerals.** B. M. Maslennikov and L. V. Romanova (State Sci. Res. Inst. of Mineral Raw Materials). *Zavod. Lab.*, 1957, **23** (11), 1327–1328.—The sample is placed in a hollow at the end of a copper electrode (6 mm diam.) and excited by means of an a.c. arc between this electrode and an upper copper electrode with a round end. The lines of B 2496·77 and 2497·73 A on a photographic plate are compared visually with standards. If the content of Na is ≮ 2%, appropriate amounts of Na must be added to the standards.
G. S. SMITH

2553. **Qualitative test for and fluorimetric determination of boric acid.** L. Sommer (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (11), 2032–2036.—Various hydroxyketones (curcumin, resacetophenone and benzoin) were studied as reagents for qualitative tests for boric acid, and benzoin in ethanolic medium was found to be the most selective and sensitive (0·04 μg of B in 0·03 ml). *Procedure*—Evaporate one drop of the sample to dryness with 0·6 *N* NaOH (one drop) in a micro-crucible, add H_2O (one drop) to the residue, cool and add an ethanolic soln. of benzoin (0·5%) (two drops). A greenish-yellow fluorescence appears in u.v. light, which is compared with a standard. There is no interference from Cl^-, Br^-, I^-, SCN^-, CN^-, $Fe(CN)_6^{4-}$, IO_3^-, BrO_3^-, ClO_3^-, NO_3^-, NO_2^-, PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ or S^{2-}; the interfering action of chromates, periodates, persulphates and ferricyanides can be prevented by reduction by heating with an excess of sulphite. The influence of various interfering cations is described and the possibility of their removal is discussed. *Procedure for fluorimetric determination*—To a neutral soln. of the sample add 0·6 *N* NaOH (0·3 ml) and an ethanolic soln. of benzoin (0·5%) (5 ml). Make up to 50 ml with ethanol (99%) and measure the fluorescence after 6 min. The conditions must be adhered to closely. The composition of the resulting chelate was studied with the use of the method of continous variation.
J. ZÝKA

2554. **Fluorimetric determination of aluminium with Pontachrome blue-black R.** Masayoshi Ishibashi, Tsunenobu Shigematsu and Yasuharu Nishikawa (Chem. Dept., Fac. of Sci., Kyoto Univ.,

Sakyo-ku). *Japan Analyst*, 1957, **6** (9), 568–571.—Weissler and White's method of fluorimetric determination of Al (*Brit. Abstr. C*, 1947, 56) was re-examined with reference to the effect of heating. Colour development is complete within 10 min. at 80° at pH 4·8 and the intensity of fluorescence remains unchanged for 2 hr. Interference results from a comparable amount of Co, Ni, Cu and Fe, but these metals are removed by electrolysis with a mercury cathode. The working curve is linear for 0·2 to 20 μg of Al in 20 ml. The fluorimeter is calibrated with quinine sulphate soln. (0·1 g per litre). K. SAITO

2555. **Spectrophotometric determination of aluminium and iron with haematoxylin.** L. Guerreschi and R. Romita (Rome University, Italy). *Ric. Sci.*, 1957, **27** (11), 3361–3380.—The effect of different variables in the spectrophotometric determination of Al by haematoxylin in the presence of Fe has been examined. By using an ammonium carbonate - bicarbonate buffer and working under the optimum conditions, both components may be determined with a standard deviation of a single measurement of $\pm$ 1·5%. L. A. O'NEILL

2556. **The precision and rapidity of certain chemical and physical determinations of alumina in aluminosilicates.** I. A. Voinovitch and J. Debras (Cent. Nat. de Res. Céram., Soc. Céramique de France, Paris). *Chim. Anal.*, 1957, **39** (11), 418–428.—Details are given of the following methods—(*i*) pptn. with excess of oxine in the presence of SiO_2 with bromatometry of the excess; (*ii*) gravimetric determination of Al_2O_3 plus TiO_2 with ammonium benzoate, after removal of SiO_2 and reduction of Fe_2O_3; (*iii*) pptn. with aq. NH_3 after removal of SiO_2 by double dehydration with HCl; (*iv*) pptn. with aq. NH_3 after a single dehydration of SiO_2 with HCl and removal with gelatin soln.; (*v*) spectrophotometric determination with ferron; (*vi*) quantitative spectrography. Figures are given for replicate determinations in several clay, etc., samples, in synthetic soln. which contain TiO_2 and Fe_2O_3, and in A.S.T.M. materials, together with some full analyses of clays. Reproducibilities for the various methods, which vary according to the substance analysed, were—(*i*) and (*ii*), $\pm$ 0·1 to 0·6%; (*iii*) and (*iv*), $\pm$ 0·2 to 1·0%; (*v*) $\pm$ 0·1 to 1·5%; (*vi*) $\pm$ 0·3 to 1·0%. It is concluded that method (*vi*) is the most rapid and specific. Method (*v*) needs more study with respect to interferences, but is rapid and useful for analyses in series; (*i*) is the most rapid of the chemical methods studied and is precise and reproducible; and (*ii*) is the method of choice when speed is not the main consideration. The classical NH_3 procedures are the most simple. With suitable precautions they give reproducible results which are, however, systematically high. R. E. ESSERY

2557. **Amperometric titration of indium with Complexone [III].** V. M. Vladimirova. *Zavod. Lab.*, 1957, **23** (11), 1286–1289.—The soln. containing In is mixed with 10 to 15 ml of conc. HCl and 5 ml of conc. H_2SO_4 and evaporated to fuming. The residue is boiled with 100 ml of water and the ppt. ($PbSO_4$) is filtered off after 2 hr. and washed with 1% H_2SO_4. The filtrate at 60° to 80° is treated with 5 g of NH_4Cl and then with excess of aq. NH_3 to precipitate hydroxides. The ppt., after having been collected and washed with 2% NH_4Cl soln. containing aq. NH_3, is dissolved in hot dil. HCl (1 : 3) and the soln. is diluted to 50 or 100 ml. An aliquot (5 to 10 ml) is treated with 0·5 to 1·0 g of tartaric acid (to prevent interference of Sn and Sb), 1 to 2 ml of ascorbic acid (to reduce Fe^{3+}) and 0·2 ml of 5% thiourea soln. (to prevent interference of Cu), then with aq. NH_3 to neutralise the soln. to Tropaeolin OO, and finally with 15 to 20 ml of buffer soln. (pH 1) (50 ml of 0·2 *M* KCl and 97 ml of 0·2 *N* HCl diluted to 200 ml). The soln. is titrated amperometrically on the dropping-mercury electrode at $-$ 0·7 V *vs.* the S.C.E. with 0·005 *M* EDTA (disodium salt). Interference is caused by the presence of Bi and As. G. S. SMITH

2558. **Colorimetric determination of thallium.** G. V. Efremov and V. A. Galibin. *Uch. Zap. LGU*, 1957, (211), 83–86; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,344.—The use of certain dyes of the fuchsine (**I**) and Malachite green (**II**) groups for the photometric determination of Tl has been studied. The ion $TlCl_4^-$ does not give coloured compounds with **I**, parafuchsine, Aniline blue, Alkali blue, Setoglaucine, Setocyanine or Chrome green; it gives coloured compounds, extractable with benzene, with Methyl green (**III**), Alkali Brilliant green (**IV**) and Turquoise blue (**V**). The reaction of $TlCl_4^-$ with **III** is reversible and so cannot be used for the photometric determination of Tl. The use of **II**, **IV** and **V** is convenient for determining Tl, since smaller quantities of Tl (0·3 μg per ml) may be determined than with methyl violet. The amounts of Tl which may be determined with **II**, **IV**, **V** and Crystal violet are, respectively, 0·3 to 2·3, 0·4 to 2·5, 0·2 to 2·0, and 0·5 to 2·7 μg per ml. C. D. KOPKIN

2559. **Titrations with quinol and analogous reducing agents. VI. Utilisation of the reaction between cerium(IV) and manganese(II) salts.** L. Mráz, V. Simon and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1957, **51** (10), 1828–1831.—In slightly acid soln. Ce^{4+} react quant. with Mn^{2+} according to the equation—$2Ce^{4+} + Mn^{2+} + 2H_2O = 2Ce^{3+} + MnO_2 + 4H^+$; the resulting Mn^{4+} can be titrated with quinol soln., or complexometrically after having been reduced with hydroxylamine. *Procedure*—To the soln. of the sample (containing 50 to 200 mg of Ce^{4+} and 0·2 to 0·4 *N* H_2SO_4) add K_2SO_4 (satd. soln.) (20 ml); the total vol. should not exceed 30 to 40 ml. Heat and add 0·1 *N* $MnSO_4$ (20 ml), heat again, cool, and filter off the ppt. on paper. Wash the ppt. into the flask where the pptn. has been carried out with H_2O, 4 *N* H_2SO_4 and 5 to 15 ml of 0·1 *N* quinol (exactly); mix, dilute to 2 *N* H_2SO_4 and titrate with 0·1 *N* $Ce(SO_4)_2$ (ferroin as indicator, or potentiometric control). Alternatively, wash the ppt. into the titration flask with H_2O and hydroxylamine sulphate soln., add 0·1 *N* EDTA (disodium salt) (10·00 ml), aq. NH_3 - NH_4Cl buffer soln. (pH 10), and Eriochrome black T as indicator, and titrate with 0·1 *M* $MgSO_4$. Vanadate and dichromate do not interfere. J. ZÝKA

2560. **Reaction of 8-quinolinol and 2-methyl-8-quinolinol with rare-earth elements.** W. W. Wendlandt (Texas Technol. Coll., Lubbock, U.S.A.). *Science*, 1957, **125**, 1042–1043.—The sensitivity of the reaction between 8-quinolinol (8-hydroxyquinoline) (**I**) and 2-methyl-**I** with La, Ce^{III}, Pr, Nd, Sm, Gd, Y and Sc was determined at pH 9·5. The reaction sensitivities in μg per ml for **I** and

2-methyl-**I**, respectively, are—La 0·91, 36; Ce 0·93, 18; Pr, 3·7, 37; Nd, 3·7, 37; Sm, 1·9, 39; Gd, 1·0, 6·0; Y, 0·57, 23; Sc, 1·2, 2·9. CHEM. ABSTR.

2561. **Spectrographic method for the determination of rarer elements in silicates.** C. O. Harvey and K. L. H. Murray (Geological Survey and Museum, Exhibition Rd., London). *Analyst*, 1958, **83**, 136–143.—In the general method described, the sample is buffered with $CaSO_4$ which, at the temp. of the arc, will rapidly decompose the minerals and, being relatively non-volatile, will persist in the arc gases until the "burn" is completed. The Ca atom line at 314·078 mμ is used as the internal standard control line, comparison with the analysis lines being made at constant photographic density. Carefully selected spectrum lines suitable for determinations of the rarer elements in silicate rocks and minerals are listed with appropriate comments. These are not necessarily the most sensitive lines, either because interference by (CN) bands or by emission from another element is likely, or because the most sensitive line is not located within the chosen range, *viz*, 275 to 467 mμ. Details of the method of recording the spectra are given. A method for preparing $CaSO_4$ free from the traces of Ba and Sr that occur in normally obtainable pure $CaSO_4$ is described.

A. O. JONES

2562. **Chemical isolation and spectrographic determination of certain rare earths in purified thorium and uranium preparations.** C. Feldman and J. Y. Ellenburg (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 418–422.—Microgram amounts of Ce, Dy, Eu, Gd, La, Nd and Sm can be quant. recovered from $Th(NO_3)_4.12H_2O$ and $UO_2(NO_3)_2.6H_2O$ by dissolving the salt in an 11·1% (v/v) conc. HNO_3 - diethyl (or di-*n*-propyl) ether mixture, rapidly stirring the soln. for ≃ 10 min. with conditioned cellulose (2 g), and then filtering through a fritted-glass disc (coarse porosity). The rare earths are removed from the cellulose with aq. HNO_3 (100 ml) of pH 2; the soln. is adjusted to pH 1 with dil. HNO_3 (pH 2), and Fe, Zr, Sc and residual Th are then removed by extraction at 60° into 0·5 *M* thenoyltrifluoroacetone in xylene. The aq. phase is washed with xylene, adjusted to pH 4·5, and the rare earths are extracted into a fresh portion of thenoyltrifluoroacetone, from which they are brought into aq. soln. by shaking for ≃ 5 min. with *M* HCl (15 ml) at 60°. The rare earths (including Y) can be determined spectrographically (in nitrate form) on graphite electrodes in an argon - oxygen atm. with Pd as internal standard and $Zn(NO_3)_2$ as buffer (to suppress the matrix effects of Ce and La). Max. sensitivity (from 0·00025 p.p.m. of Y to 0·01 p.p.m. of Ce, Nd or Sm) can be attained by evaporating 1 ml of soln. (≡ 20 g of Th) on one pair of electrodes. When Ce and La are absent, spectrographic recoveries range from 98 to 102%. W. J. BAKER

2563. **A rapid modified method for the determination of carbon-14.** J. Horáček and D. Grünberger (Anal. Lab., Chem. Inst., Acad. Sci., Prague). *Chem. Listy*, 1957, **51** (10), 1944–1946.—The sample is ignited according to Körbl's method (*Chem. Listy*, 1955, **49**, 858, 862, 1532, 1664), and the CO_2 is absorbed in a novel apparatus and determined acidimetrically. The carbonate is then pptd. with $BaCl_2$ soln. and its activity measured with the use of a Geiger - Müller tube. J. ZÝKA

2564. **Quantitative estimation of graphite in refractory carbon deposits by X-ray technique.** W. A. Frad and P. G. Herold (School of Mines and Metall., Rolla, Mo., U.S.A.). *Nature*, 1957, **180**, 1273–1275.—Graphite in carbon deposits produced by the attack of CO on refractories is determined by means of X-ray spectrometer readings, with fluorite as an internal standard and the technique of McCreery (*J. Amer. Ceram. Soc.*, 1949, **32**, 141) for preparing standards and minimising errors. With a series of standards, each containing 40% of fluorite and increasing amounts of graphite, the ratio H_g/H_f of the height above background of the graphite line at 3·38 A to the corresponding height of the fluorite line at 3·16 A is plotted against percentage of graphite (by wt.), to give the standard curve. This is a straight line above 7% of graphite, but deviates from linearity below that level. Graphite was determined in amounts as small as 0·1%, with a relative error of ± 10% when automatic recording was used. R. E. ESSERY

2565. **Indirect absorptiometric determination of cyanide.** O. Alcides Ohlweiler and J. Oliveira Meditsch (Escola de Engenharia, Porto Alegre, Brazil). *Anal. Chem.*, 1958, **30** (3), 450–451.—The colorimetric method described previously (*cf. Anal. Abstr.*, 1954, **1**, 2632), based on the reaction of Hg^{2+} with *p*-dimethylaminobenzylidenerhodanine has been improved to extend the lower range to 0·15 μg of CN^- per 3 ml and to avoid interference by S^{2-}. Up to 150 μg of S^{2-} per ml can be removed by addition to the sample (5 ml) of 20% aq. $Cd(NO_3)_2$ soln. (0·2 ml). The filtrate is acidified with tartaric acid and, after micro-diffusion of CN^- to prevent interference by SCN^-, the colour is developed and the extinction is measured at 470 mμ. Concn. < 1·5 μg are determined by the differential technique. W. J. BAKER

2566. **The effect of sulphuric acid on the determination of a small amount of germanium.** Hiroshi Nishida (Ind. Training Inst., Iwate Prefecture, Uchimaru, Morioka). *Japan Analyst*, 1957, **6** (10), 654–658.—An aqueous soln. of GeO_2 (> 1 mg of Ge) produces a white ppt. when heated with H_2SO_4 to white fumes. This ppt. is insol. in water, but sol. in HCl and alkali. In the presence of silicic acid, GeO_2 is readily co-pptd. with SiO_2 and remains insol. in HCl or alkali; the amount co-pptd. increases with increase in the amount of SiO_2 pptd. and with increased concn. of H_2SO_4.

K. SAITO

2567. **Rapid methods for the analysis of metals and mineral raw materials. I. Polarographic determination of germanium.** Z. Šulcek and J. Gottfried (Centr. Geolog. Inst., Prague). *Chem. Listy*, 1957, **51** (11), 2010–2016.—*Procedure for sphalerite (natural ZnS)*—Decompose the sample (2 to 5 g) with 10 to 30 ml of dil. HNO_3 (1:1) and H_2SO_4 (1:1). Evaporate twice with H_2SO_4 to remove nitrates. Dilute the residue with water, cool, transfer to a distillation apparatus, neutralise with conc. NaOH soln., add HCl and distil. Make up the distillate with conc. NaOH soln. to 50 ml, measure 20 ml into a 50-ml flask, neutralise with NaOH soln. and add dil. H_2SO_4 till slightly acid. Add 2 *M* Na_2CO_3 (3 ml), starch soln. (1%) (0·5 to 1 ml) and 0·1 *N* iodine, dropwise, till a blue colour appears (As^{III} to As^{V}). Add gelatin (0·05%) (0·5 ml) and 0·1 *M* EDTA (disodium salt) (5 ml), adjust the vol., remove O with a stream of N, and register the polarographic wave from − 1·0 V.

Evaluate the result with the use of the method of standard addition. When determining Ge in gas-works ash, the sample must first be fused with an excess of NaOH and Na_2O_2 in a nickel crucible. A detailed procedure is given. The described method is suitable for samples containing $> 0{\cdot}009\%$ of Ge. The results were in good agreement with those obtained with the photometric method.

J. ZÝKA

2568. **Use of naphthalene derivatives in inorganic analysis. III. The nitroaminonaphthalene monosulphonic acids as spot tests for stannous tin.** J. R. A. Anderson and J. L. Garnett (N.S.W. Univ. of Technol., Sydney, Australia). *Anal. Chim. Acta*, 1957, **17** (5), 452–458 (in English).—Three compounds isomeric with 6-nitro-2-naphthylamine-8-sulphonic acid have been synthesised and found to be specific spot reagents for Sn^{2+}. These reagents are ammonium 8-nitro-2-naphthylamine-6-sulphonate and the potassium salts of the two nitronaphthylaminesulphonic acids prepared by the mononitration of 2-naphthylamine-5-sulphonic acid. To test for Sn^{2+}, spots of aq. soln. of metal ions on paper are sprayed with a 0·1% soln. of any one of the reagents, air-dried and examined for fluorescence under u.v. The papers are then sprayed with 15 *N* aq. NH_3, air-dried and again examined under u.v. for quenching of any previous fluorescence. Only Sn^{2+} show strong fluorescence after the treatment with aq. NH_3. The limit of detection with each reagent is 10^{-8} g of Sn^{2+}. The previously described reagent 6-nitro-2-naphthylamine-8-sulphonic acid (ammonium salt) (*cf. Anal. Chim. Acta*, 1953, **8**, 393; 1956, **15**, 246) gives a stronger fluorescence and has a detection limit of 10^{-7} g of Sn^{2+}. The synthesis of the reagents is described.

G. BURGER

2569. **A new volumetric method for determination of tin in the presence of antimony.** J. V. Villadsen and K. G. Poulsen (Tech. Univ. of Denmark, Copenhagen). *Acta Chem. Scand.*, 1957, **11** (10), 1671–1676.—*Procedure*—The sample soln. is oxidised by bromate titration (*cf.* Györy, *Z. anal. Chem.*, 1893, **32**, 415) so that it contains Sn^{4+} and Sb^{5+}. Aliquots containing 0·15 g of Sn are taken and 7·5 g of oxalic acid (to prevent pptn. of SnS_2) and 20 ml of conc. HCl are added. The soln. is diluted to 100 ml and boiled with 0·3 g of thioacetamide for each 0·1 g of Sb present. Hot water is added (100 ml) and, after cooling to 50°, the Sb_2S_3 is filtered off. The filtrate and washings (with 0·1% oxalic acid) are treated with 17 g of $(NH_4)_2S_2O_8$ to destroy the oxalic acid and are heated for 15 to 20 min. to destroy the excess of $S_2O_8^{2-}$. The Sn may then be determined by established procedures, and in this investigation was determined by reducing with Al to metallic Sn, which is dissolved in HCl - H_2SO_4 and the Sn^{2+} are titrated with bromate, with starch - iodide as indicator. An atmosphere of CO_2 is maintained over the soln. being titrated. Various possible sources of error, including the rate of decomposition of the persulphate, are investigated. The determination takes 2 to 2·5 hr., and has a mean deviation of $\pm$ 0·2%.

E. J. H. BIRCH

2570. **Coulometric reduction of oxides on tin-plate.** R. P. Frankenthal, T. J. Butler and R. T. Davis, jun. (U.S. Steel Corp., Monroeville, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 441–443.—The concn. of oxides as determined by coulometric reduction on tin-plate surfaces is influenced by the composition and buffering capacity of the electrolyte, by the O dissolved therein, and by the pH and current density. Oxide-film values determined in 0·1 *M* KCl are always lower than those determined in 0·001 *M* HCl. Electrolytes of pH 3 and 4 and buffered electrolytes of pH 5 to 7 give similar values, but plain electrolytes of pH 5 to 7 and all basic electrolytes give lower values (probably because of dissolution of an alkali-sol. intermediate hydroxide). The curve of oxide-film values *vs.* current density (0·02 to 0·39 mA per sq. cm) is linear. Dissolved O in the electrolyte causes a positive error proportional to (electrolysis time)$^{0{\cdot}5}$.

W. J. BAKER

2571. **Chromate method for determining small quantities of lead.** I. E. Starik and F. E. Starik. *Trudy Radiev. Inst., Akad. Nauk, SSSR*, 1957, **5** (2), 129–133; *Ref. Zhur., Khim.*, 1957, Abstr. No. 66,400.—A method is described for the separation and determination of small amounts of Pb in water and readily soluble minerals and rocks. Treat the material with HCl, remove the insoluble residue, and to the filtrate add ammonium acetate, citric acid (to eliminate interference from Fe) and a soln. of $(NH_4)_2Cr_2O_7$; dissolve the resulting ppt. in HCl, add ethanol to the soln. to reduce $Cr_2O_7^{2-}$, evaporate the soln. to dryness, dissolve the residue in a 10% soln. of K Na tartrate in *N* HNO_3 and determine by polarography. The method allows the separation of up to 90% of the Pb when other methods are not suitable and can be used to determine Pb without electrolytic separation of Cr.

C. D. KOPKIN

2572. **Determination of lead by dithizone in a single-phase water - acetone system.** D. G. M. Diaper and A. Kuksis (Royal Military Coll. of Canada, Kingston, Ontario). *Canad. J. Chem.*, 1957, **35** (11), 1278–1284.—The usual determination of Pb by dithizone is modified to avoid extraction by CCl_4. Aq. acetone (70%) is used as solvent, and this dissolves the Pb dithizonate complex as well as the complexing salts (KCN and hydroxylamine hydrochloride) and barbitone buffer used. Absorption measurements are made at 500 mμ. Results obey the Beer - Lambert law. The average difference between duplicates is 0·11%, and the coeff. of variation is 1·93%, with lead standards up to 10 μg, in 32 determinations. Only Cu was tested for interference. By increasing the cyanide concn. recommended in the procedure four times, about 25 μg of Cu gives the same effect as 1 μg of Pb. Possible interference from Sn^{II}, Tl^{I}, Bi, Hg and Ag was not investigated quantitatively. The method is limited by a narrow range of pH (optimum 5·5), and by the inability of the aq. acetone to dissolve large amounts of complexing salts.

P. M. SORGO

2573. **Preparation of the sample for chemical analysis of titanium sponge.** Kazukiyo Ohashi, Tsuyoshi Nakayama and Kameji Shimasaki (Osaka Titanium Co., Higashihama, Amagasaki). *Japan Analyst*, 1957, **6** (9), 572–579.—The sampling of titanium sponge was studied with reference to the grain size and the segregation of impurities. A well-mixed sample of titanium sponge (900 g) is pressed on a die (diam. 70 mm) into a cylinder, which is drilled at the centre (145 r.p.m.; rate, 1·45 to 3·45 mm per min.) to give a hole of 50 mm diam. The drillings are used for chemical analysis, except for determinations of H_2O, O or H. No marked nitriding takes place with such slow drilling.

K. SAITO

2574. **Arsenate method for the iodimetric determination of titanium.** G. B. Shakhtakhtinskiĭ and A. M. Mukimov. *Me'ruzeler. AzerbSSR Elmler Akad., Dokl. Akad. Nauk, AzerbSSR*, 1957, **13** (6), 629–632; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,353.—The method described is based on the pptn. of Ti as arsenate, solution of the ppt. in HCl and H_2SO_4, and iodimetric titration of the AsO_4^{3-} liberated. C. D. KOPKIN

2575. **Spectrophotometric determination of titanium with salicylamidoxime.** D. Banerjea (Dept. of Inorg. Chem., Indian Ass. for Cultiv. of Sci., Calcutta). *Z. anal. Chem.*, 1957, **159** (2), 123–128 (in English).—The titanium complex of salicylamidoxime is extracted from aq. soln. at pH 4·5 to 7·0 with *iso*butyl alcohol. For the reaction to be quant., the ratio of salicylamidoxime to Ti must be $< 50:1$. The extinction of the extract is measured at 400 mμ, and Beer's law is obeyed over the range 0·25 to 15 μg of Ti per ml. Chloride, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and UO_2^{2+} do not interfere. Copper can be masked by the addition of thiourea, but Fe^{III}, V^{III}, Mo^{VI}, W^{VI}, cations that undergo extensive hydrolysis in the acetate buffer medium, tartrate, oxalate and PO_4^{3-} interfere. J. H. WATON

2576. **Determination of large quantities of titanium by polarography.** N. S. Gertseva and E. A. Khomyakova. *Trudy Inst. Metallurg., Akad. Nauk, SSSR*, 1957, (1), 241–244; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,354.—Dissolve the sample in HF and H_2SO_4, remove HF, dissolve the residue in dil. HCl and make up to a known volume. Evaporate a suitable aliquot, depending on the content of Ti, to 2 or 3 ml, cool, transfer to a 50-ml flask and add 40 ml of background soln. [dissolve 18·6 g of EDTA (disodium salt) in 800 ml of water and 1 to 1·5 ml of 25% aq. NH_3, add 272 g of Na acetate and 15 ml of conc. H_2SO_4; filter the soln. and make up to 1 litre]. After 10 min. neutralise with aq. NH_3 to methyl red, cool, make up to the mark and polarograph. The calculation is carried out by the method of additions. The relative error in determining Ti in various products is $> 3\%$. With concn. of Ti < 5 mg per litre the method is not accurate. With concn. of Ti of about 40 to 500 mg per litre, the Ilkovic equation is accurately followed. Interference is caused by Cu, V, Pb and Fe in amounts greater than six times that of Ti. Lead may be first pptd. as $PbSO_4$. The main bulk of Fe and Cu is removed on the mercury cathode. If V is present, fuse the sample with Na_2CO_3 and extract the melt with hot water. The described method is recommended for the rapid analysis of titanomagnetite ores, concentrates and slags containing 50 to 60% of TiO_2. C. D. KOPKIN

2577. **Quantitative separation of titanium from molybdenum and vanadium by ion-exchange chromatography.** I. P. Alimarin and A. M. Medvedeva. *Trudy Moskov. Inst. Tonkoĭ Khim. Tekhnol.*, 1956, (6), 3–8; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,672.—A method is evolved for the quant. chromatographic separation of Ti from Mo and V, which interfere in the determination of Ti as the oxide, by the use of the resin SBS, first converted to the H form by treatment with 10% HCl. The diameter of the grains is 0·5 to 1 mm, the diameter of the column is 1 cm, and the rate of elution is 3 ml per min. The influence of the acidity of the soln., the character of the anion of the acid and the concn. of H_2O_2 on the adsorption of Ti is studied. The adsorption of Ti in relation to the nature of the anion of the acid decreases in the following order, because of the increase of the stability of the complex anion formed—$ClO_4^- > Cl^- > SO_4^{2-}$. The adsorption of Ti is a maximum at an acidity of 0 to 0·6 *N* and decreases sharply with increase of the acidity to 1·2 *N*. A 1% soln. of H_2O_2 is sufficient to separate Ti from Mo and V, forming complex anions in weakly acid soln. (pH 1) which are not adsorbed. The abs. error in determining Ti is $> 0{\cdot}5\%$. C. D. KOPKIN

2578. **Determination of oxygen in titanium. Modified vacuum-fusion apparatus and platinum-bath technique.** S. J. Bennett and L. C. Covington (Titanium Metals Corp., Henderson, Nev., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 363–365.—In the improved arrangement described, the Pyrex-glass furnace is lined with a removable quartz sleeve, and has a quartz cup to hold the quartz thimble containing the graphite crucible and powder. There is also an inlet for insertion of single samples, and a 3-stage Toepler pump for rapid evacuation of the gases. The CO formed is oxidised to CO_2, which is then absorbed in Ascarite. The platinum-bath procedure (*cf. Anal. Abstr.*, 1957, **4**, 864) is used, the furnace being kept at 1900° during the run. Initial out-gassing is complete in $\simeq 1$ hr. at 2400°, 30 samples can be analysed before opening the system to the air, and the standard deviation is from 0·001 to 0·005%. Tin, Al, Mn, Cr, V, Mo, Zr, Ni and Fe do not interfere. W. J. BAKER

2579. **Electrolytic separation of iron from titanium.** V. A. Belyaeva, M. I. Tarantsova and E. I. Glushko. *Sb. Stud. Rabot, Rostovsk. Univ.*, 1957, (3), 45–48; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,363.—The conditions for the electrolytic separation of Fe and Ti were studied by the use of artificial mixtures and industrial samples. It was found that the optimum conditions are—current strength 2·5 to 3 amp., voltage 5 to 6 V. The possibility is indicated of the colorimetric determination of small quantities of Ti by the peroxide method after the preliminary removal of Fe. It is established that the most convenient method of dissolving the sample is by solution in aqua regia with the addition of a few drops of HF. The time required for the electrolytic separation of Fe and Ti (including the dissolution of the sample) and the colorimetric determination of Ti is about 3 hr. C. D. KOPKIN

2580. **Spectrographic determination of impurities in titanium.** L. N. Filimonov, A. I. Essen and Z. A. Zakharova (Giprotsvetmetobrabotka Inst.). *Zavod. Lab.*, 1957, **23** (11), 1313–1315.—The sample is oxidised to TiO_2 at 1100° and mixed with an equal wt. of CuO. The mixture is pressed into a briquette, which is placed in the end of a graphite rod and excited in an arc with copper as the other electrode. The mixing with CuO assists the passage and continuance of the arc. Many impurities in concn. of $\simeq 0{\cdot}01\%$ and above can be determined against synthetic standards. G. S. SMITH

2581. **Determination of silicon and phosphorus in titanium dioxide by spectrographic analysis.** M. P. Atroshenko and M. S. Kozyreva. *Zavod. Lab.*, 1957, **23** (11), 1317–1320.—An a.c. arc is used with samples mixed with NiO which serves both to stabilise the arc process and to provide an internal standard for the determination of Si, the

lines Si I 2514·3 and Ni I 2540 A being measured. The determination of P is carried out with a higher current, 20 amp., and the absolute blackening of the line P I 2553·28 A is measured. The three-standard method is used. G. S. SMITH

2582. **Spectrographic analysis of titanium-base alloys.** K. A. Moiseeva, K. A. Sukhenko, S. I. Mladentseva and A. V. Aksenova. *Zavod. Lab.*, 1957, **23** (11), 1316.—With spark excitation for determination of Al, Cr and Fe in titanium alloys, structural differences between cast and wrought samples have no effect on the analytical results obtained; similarly with arc excitation for determination of Si. The line pairs (in A) are—Al 3961·53, Ti 3989·76; Cr 2843·25, Ti 2841·94; Al 3092·71, Ti 3048·77; Cr 2766·54, Ti 2841·94; Fe 2599·40, Ti 2555·99; Si 2881·57, Ti 2901·94; Si 2881·57, Ti 2841·93. The samples are in the form of rods and the other electrode is a carbon rod with a hemispherical end. G. S. SMITH

2583. **Volumetric determination of zirconium. (Preliminary communication.)** A. Schneer and H. Hartmann (Inst. for Gen. and Inorg. Chem., Loránd Eötvös Sci. Univ., Budapest). *Magyar Kém. Foly.*, 1957, **63** (10), 295–296.—Precipitate Zr as a salt of mandelic acid (**I**) from a 6 *N* HCl soln. Collect the ppt. on a glass filter and dissolve it with almost saturated Na_2CO_3 soln. Add 23% NaOH soln. (5 to 15 ml) and an excess of 0·5 *N* $KMnO_4$. After keeping the soln. at room temp. for 10 to 15 min., dilute it, then acidify it with dil. H_2SO_4 and add a slight excess of 0·5 *N* oxalic acid and titrate at 60° with 0·1 *N* $KMnO_4$. The blank is determined in the absence of the zirconium salt of **I**. The relative error is $\pm$ 1% if 2 to 50 mg of Zr is present. *p*-Bromomandelic acid (**II**) can be used instead of **I**. Since 98·53% of **I** or **II** is oxidised to benzoic acid and 1·47% to H_2O and CO_2, then 1 ml of 0·1 *N* $KMnO_4$ $\equiv$ 0·5136 mg of Zr. For smaller amounts, dissolve the zirconium salt of **I** with conc. H_2SO_4 at 95° and keep in 69 to 98% by wt. H_2SO_4 containing $Na_2Cr_2O_7$ at 90° to 100° for 20 min. Dilute the soln. and back-titrate with $FeSO_4$ soln., with ferroin as indicator. If 1 to 5 mg of Zr is present, the relative error is $-$ 1 to $-$ 2%; if $<$ 1 mg is present, the relative error is $-$ 2 to $-$ 5%. A. G. PETO

2584. **Micro-determination of zirconium in sulphuric acid solutions with catechol violet.** J. P. Young, J. R. French and J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 422–425.—From 0·4 to 2·8 μg of Zr per ml can be determined in the presence of Th, U, La, Ce, Fe, Ni and Cr (but not of Al, Ti or V) by measuring the extinction of the blue Zr - catechol violet complex at 640 mμ and pH 5·1. Beer's law is valid up to 2 μg of Zr per ml and the coeff. of variation is $\pm$ 2% (7 analyses); the sensitivity is twice that of the Flaschka and Farah method (*cf. Anal. Abstr.*, 1957, **4**, 453). The Th to Zr ratio should not exceed 10 unless Th is added to the reference soln.; provided that the Fe to Zr ratio is $>$ 6, interference by Fe^{2+} or Fe^{3+} can be avoided by addition of thioglycollic acid, but larger amounts of Fe should be removed initially at a mercury cathode. W. J. BAKER

2585. **Sodium dihydrogen hypophosphate as a reagent for the quantitative co-precipitation of thorium.** L. Kosta ("J. Stefan" Inst., Ljubljana, Yugoslavia). *Energia Nucleare*, 1957, **4**, 37–42 (in English).—The co-pptn. of Th was tested by adding a small amount of UX_1 tracer to an approx. 5 $\times$ 10^{-3} *M* acid soln. of the metal ion in a 50-ml centrifuge tube. After the addition of 5 ml of 0·06 *M* $Na_2H_2P_2O_6$ the vol. was adjusted to 35 ml and the soln. was heated to boiling with constant stirring. The ppt. was allowed to settle and was then centrifuged. The supernatant soln. was decanted through a filter into a 50-ml flask. The ppt. was washed with 10 ml of the acid being tested and the wash soln. was added to the filtrate. The ppt. was dissolved and the soln. diluted to a known vol. Aliquots of the two soln. were counted with a Geiger - Müller counter. In 2 *M* $HClO_4$, HNO_3, HCl and *M* H_2SO_4, Zr and Ti carry 99% of UX_1; Bi and Sn^{4+} carry 99% of UX_1 from 2 *M* $HClO_4$, and Fe^{3+} carries 96%. A good method for the separation of Th from most ions consists in pptg. $Bi_4(P_2O_6)_3$ in 2 *M* $HClO_4$. On being boiled, the gelatinous ppt. coagulates and settles rapidly. It crystallises after several hours. The ppt. can be decomposed and the Bi reduced to the metallic state with alkaline stannite or with an alkaline formaldehyde soln. The metal holds Th quant. adsorbed on the surface and can be washed with NaOH soln. without loss of Th. This procedure eliminates all ions other than Bi and Th in the final soln. CHEM. ABSTR.

2586. **Complexometric titrations (chelatometry). XXXIV. Chrome azurol S as an indicator for the determination of thorium, nickel, cerium and lanthanum.** M. Malát and M. Tenorová (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1957, **51** (11), 2135–2137.—*Thorium*—To a soln. of the sample containing 2 to 220 mg of Th add 6 to 8 drops of indicator (0·1% aq. soln.) and HNO_3 to pH 1 to 2, make up to 100 ml, and titrate with EDTA (disodium salt) soln. (**I**) to a colour change from red - violet to yellow. There is no interference from Na, K, Li, Rb, Cs, Ca, Sr, Ba, Mg, Ag, Mn, Zn, Cd or Tl. The interference of Fe^{3+} and Hg^{2+} can be avoided by the addition of ascorbic acid. The interference of other cations and anions is discussed. *Nickel*—To the sample containing 3 to 24 mg of Ni add 6 to 8 drops of indicator and dil. aq. NH_3 till the violet colour of the complex of Ni with the indicator appears; then add pyridine (1 to 2 ml) and titrate with **I** as described above. Alkaline earths and Mg are titrated in the same manner. *Cerium and lanthanum*—Amounts of $>$ 75 mg of Ce and 85 mg of La in 100 ml of soln. can be determined as described under Th. Rare-earth elements interfere. A 0·1% aq. soln. of Chrome azurol S was used as the indicator. J. ZÝKA

2587. **Colour test for nitrates employing Michler's ketone.** L. S. Malowan (Univ. of Panama, Panama City). *Chemist Analyst*, 1957, **46** (3), 67.—Michler's ketone (**I**) in H_2SO_4 gives a yellow colour with organic and inorganic nitrates, *e.g.*, $Ba(NO_3)_2$, $Co(NO_3)_2$, $Bi(NO_3)_3$, and erythritol tetranitrate. Peroxides, hypochlorites, ClO_3^-, IO_3^- and $S_2O_8^{2-}$ do not interfere. Dissolve 0·025 g of **I** in 1 ml of conc. H_2SO_4 in a test-tube, add the sample, place in an 80° water bath for 5 min., and dilute with 20 ml of cold H_2O. A brilliant yellow colour appears, with slightly green fluorescence, sometimes with a small yellow ppt. Alternatively, place a few milligrams of **I** on a spot plate, dissolve in 3 drops of conc. H_2SO_4, add 0·001 g of sample and after a few minutes add 1 ml of H_2O; a yellow colour is given. R. L. MORTLOCK

2588. **Colorimetric determination of a small amount of phosphorus by the molybdenum blue method with quinol.** Takero Sudo, Taturo Hamakawa and Mitugu Kubota (Kurosaki Factory, Mitsubishi Chem. Ind., Yawata). *Japan Analyst*, 1957, **6** (9), 564–568.—The use of quinol (**I**) for the reduction of molybdophosphoric acid was studied in the absence of other reducing agents. The extinction of the molybdenum blue increases with temp. for a given period of heating; at $> 60°$, however, the excess of ammonium molybdate is also reduced. The colour develops completely within 20 min. at 50° to 60° and the intensity of colour remains unchanged for 2 hr. The sample soln. ($\simeq$ 20 ml) containing 2 to 20 μg of P is mixed with ammonium molybdate (25 g of commercial ammonium molybdate and 75 ml of conc. H_2SO_4 per 500 ml) (2 ml) and, after a few minutes, with 0·5% aq. **I** soln. The mixture is made up to 25 ml, heated in a water bath (50° to 60°) for $\simeq$ 20 min., and then measured photometrically at 660 mμ. The error is $<$ 0·5% for 1 p.p.m. of P in water.
K. Saito

2589. **Rapid determination of phosphorus in ferrophosphorus.** Shigeo Wakamatsu (Toto Seiko Co., Minamisunamachi, Koto-ku, Tokyo). *Japan Analyst*, 1957, **6** (9), 579–583.—A rapid ($\simeq$ 20 min.) determination of P in ferrophosphorus ($\simeq$ 20%) is carried out by the pptn. of P with a known amount of Mg followed by EDTA titration of the excess of Mg. When the EDTA titration is made in the presence of pptd. magnesium phosphate, the indicator, Eriochrome black T, reverts to its red colour 30 to 60 sec. after the termination of the titration. The pptn. of P is satisfactory for > 5 mg of P in the presence of more than a 5-mg excess of Mg^{2+}. Fusion with Na_2O_2 at 800° ensures rapid decomposition of the sample. Interference resulting from other ingredients is masked by the addition of tartaric acid and KCN. The error is $\simeq$ 0·1% (absolute). *Procedure*—Fuse the sample (0·5 g) with Na_2O_2 for 5 min., cool, dissolve in water (100 ml), boil for 2 min. and dilute to 500 ml. To a 50-ml portion add HCl (10 ml) and tartaric acid (10%, 5 ml), neutralise with aq. NH_3 soln. and add KCN (20%, 5 ml), magnesium soln. (8·5 g of $MgCl_2.6H_2O$ and 17 g of NH_4Cl in 800 ml of water is neutralised with aq. NH_3 soln., filtered, acidified to pH 5 to 6 and diluted to 1 litre) (25 to 30 ml) and aq. NH_3 soln. to give a pH of 10. After 5 min. (without filtration) add the indicator (0·2% in ethanol, a few drops) and titrate rapidly with 0·03 *M* EDTA, until a greenish-blue colour appears.
K. Saito

2590. **Separation and identification of acids by paper chromatography. III. The water-soluble inorganic phosphates.** L. C. Mitchell (Div. Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1038–1050.—For the paper-chromatographic separation of water-soluble ortho-, pyro-, tri-, trimeta- and tetrameta-phosphates, a mixture of *n*-butanol (25 ml), 7% v/v aq. pyridine (10 ml), acetone (50 ml), 10% v/v aq. HNO_3 (10 ml) and H_2O (to 100 ml) is used as mobile solvent. The phosphates are detected by spraying with ammonium molybdate (1 g) and HCl (20 ml) in ethanol (to 200 ml), air-drying overnight, and then lightly overspraying with benzidine (0·4 g), aq. NH_3 (10 ml) and H_2O (30 ml) in ethanol (to 200 ml). Chromatograms showing distinctive characteristics of the phosphates are reproduced.
A. A. Eldridge

2591. **Volumetric determination of arsenic as quinoline molybdoarsenate.** S. Meyer and O. G. Koch (Neunkircher Eisenwerk A.-G., Neunkirchen/Saar). *Z. anal. Chem.*, 1957, **158** (6), 434–438.—Small amounts of As may be determined rapidly (20 min.) by pptn. of quinoline molybdoarsenate followed by titration of the ppt. The reproducibility is $\simeq \pm 10$ μg of As. *Quinoline molybdate reagent*—Pour a soln. of sodium molybdate (250 g) in H_2O (500 ml) into aq. HCl (*d*, 1·19) (460 ml), add 30% aq. H_2O_2 (1 drop), mix with a soln. of quinoline (28 ml) in aq. HCl (1:1) (600 ml), heat to boiling-point and filter after 24 hr. *Procedure*—To an aq. soln. (50 ml, containing $<$ 10 μg of As) add $KClO_3$ (1 g) and aq. HCl (*d*, 1·19) (5 ml) and heat to boiling-point. Add 10% aq. tartaric acid soln. (20 ml) and quinoline molybdate reagent (20 ml), shake well and filter. Wash the ppt. with dil. HCl and then with H_2O until the washings are neutral. Suspend the ppt. in H_2O (50 ml), add a slight excess of 0·1 *N* NaOH, shake well, dilute to about 100 ml and titrate the excess of alkali with 0·1 *N* HCl, with phenolphthalein as indicator. Perform a blank titration.
A. R. Rogers

2592. **New photometric determination of a micro amount of antimony with fuchsine or malachite green.** Hidehiro Gotô and Yachiyo Kakita (Res. Inst. of Iron, Steel and other Metals, Tohoku Univ., Katabiracho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (10), 1521–1524.—Fuchsine (**I**) and malachite green (**II**) react with Sb^V in aq. soln. of pH 1·0 to 1·2 and 0·6 to 1·2, respectively, and the resulting complexes are extracted with amyl acetate (**III**). The extinctions at 555 and 628 mμ (for Sb - **I** and Sb - **II** complexes, respectively) are proportional to concn. for $<$ **6** μg of Sb per 5 ml. Tervalent Sb is oxidised with Ce^{IV}, and the excess of the Ce^{IV} is reduced with hydrazine. The sample is mixed with 6 *N* HCl (5 ml) and $Ce(SO_4)_2$ (2% in 2 *N* H_2SO_4) (0·3 ml); the product is treated with hydrazine sulphate (1%, 5 ml), **I** or **II** soln. (0·1%, 1 ml) and Na citrate (30%, 10·5 ml for **I**, 9 ml for **II**), and extracted with **III** (5 ml). Interference results from a trace of iodine, > 2 μg of Cu, CrO_4^{2-} or VO_3^{3-}, and > 10 μg of Mo, W, Cr^{3+} or Sn^{2+}.
K. Saito

2593. **Polarographic analysis of type metals.** A. A. Yavorovskiĭ and L. I. Galibeĭ. *Sb. Trud. Ukr. Nauch. Inst. Poligr. Prom.*, 1956, **4**, 104–126; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,410.—A review is made of the polarographic analysis of alloys containing Sn, Sb, Pb, Cu, Zn, Ni and Fe (41 references). The polarographic behaviour of Sn, Sb and Pb in HCl and H_2SO_4 in the presence and in the absence of complexing substances (citric acid, tartaric acid, EDTA, pyridine, NaF, etc.) is studied. It is shown that the use of complexing agents for the suppression of the Sn wave in the presence of Pb does not give satisfactory results. A method is evolved for the preparation of solutions of type metals and for their polarographic analysis for Sn, Sb, Fe and Cu; Pb is easily determined gravimetrically. The time for the analysis is 0·5 to 1 hr.; the accuracy is satisfactory. An improved method is also described for the determination of Ni, Cu and Zn with a smaller sample.
C. D. Kopkin

2594. **Quantitative gravimetric determination of bismuth as the Reinecke salt.** I. L. Bagbanlȳ and I. G. Guseinov. *Me'ruzeler. AzerbSSR Elmler Akad., Dokl. Akad. Nauk, AzerbSSR*, 1957, **13** (6),

633–638; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,379.—The conditions are studied for the quant. pptn. of Bi as $Bi[Cr(SCN)_4(NH_3)_2]_3$. Acidify the soln. with HNO_3 so that after the addition of precipitant the acidity of the soln. is $> 0{\cdot}2\ N$. Add 1 ml of freshly prepared 2·5% Reinecke's salt soln. for each mg of Bi expected. Stand the soln. and ppt. in an ice bath for 15 min., filter through a sintered glass crucible, wash the ppt. 2 or 3 times with a cold mixture of ethanol and benzene (1:1) or with cold anhydrous ethanol, dry at 105° to 110°, and weigh. C. D. KOPKIN

2595. **Polarographic determination of bismuth, copper and lead when present together.** N. S. Gertseva. *Trudy Inst. Metallurg., Akad. Nauk, SSSR*, 1957, (1), 238–240; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,677.—A method is evolved for the polarographic determination of Bi in the presence of a 6-fold quantity of Cu and any quantity of Pb, with simultaneous determination of the Cu and Pb. The use of gelatin and the passage of a stream of H in the determination of Bi and Pb are dispensed with; because of the buffering properties of the background it is possible to alter the acidity of the soln. within wide limits. Dissolve the sample by any means, remove excess of acid by evaporation to a small volume, cool, add 50 ml of the background soln. [tartaric acid 10% (w/v) in HCl (1:1)], dilute with water to 100 ml, mix and polarograph (the $E_{\frac{1}{4}}$ values *vs.* the S.C.E. for Bi, Cu and Pb are, respectively, − 0·12, − 0·24 and − 0·42 V). If Cu is to be determined, first determine Bi without gelatin, and then add 2 or 3 drops of 1% gelatin soln. and determine Cu. The concn. of Bi, Cu and Pb which may be determined are, respectively, 5 to 500, 10 to 150, and 1 to 350 mg per litre. C. D. KOPKIN

2596. **Ion-exchange separation in the analysis of bismuth-base alloys. II. Ternary alloys containing uranium and thorium.** G. W. C. Milner and J. H. Nunn (A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1957, **17** (5), 494–499 (in English).—The procedure described permits the determination of U and Th occurring together in bismuth alloys in the range 0·1% to 10%, the results being in good agreement with the known composition of alloys tested over the whole range. Dissolve the sample in HNO_3 and convert into the chlorides. Dissolve the chlorides in $5\ N$ HCl and pass the soln. through a column of ion-exchange resin De-Acidite FF and elute with $5\ N$ HCl. The eluate contains the Th. Recover the U from the column by eluting with $0{\cdot}2\ M$ HCl. Evaporate each eluate with $HClO_4$ and destroy any organic matter by oxidation with HNO_3. Determine Th in concn. < 1% absorptiometrically by means of thoronol; in concn. > 1% titrate a HNO_3 soln. of the residue with EDTA (disodium salt), with catechol violet as indicator. Determine U in concn. < 1% polarographically and in concn. > 1% by titration with $Ce(SO_4)_2$ after reduction with a lead reductor. G. BURGER

2597. **Colorimetric determination of vanadium.** H. Compaan [Anal. Res. Inst. T.N.O., Lange Kleiweg, Ryswijk (Z.-H.), Holland]. *Nature*, 1957, **180**, 980.—Vanadium in minerals and steel can be determined colorimetrically, after being brought into acid soln., by quant. extraction of its complex with a hydroxamic acid, *e.g.*, salicylhydroxamic acid, into di*iso*butyl ketone. Under optimum conditions, the corresponding complexes of Fe, Ti and U are not selectively extracted. W. J. BAKER

2598. **Extraction of vanadium hydroxyquinolinate.** F. G. Zharovskiĭ. *Nauk. Zap. Kiĭvs'k. Univ.*, 1956, **13** (13), 259–266; *Ref. Zhur., Khim.*, 1957, Abstr. No. 71,900.—The light absorption of vanadium 8-hydroxyquinolinate (**I**) is studied in various organic solvents, and it is concluded that the change in colour and intensity of colour of the soln. is due to solvation. The mol. extinction coeff. of soln. of **I** in various solvents increases in the order xylene < toluene < benzene < dichloroethane < *n*-butanol < $CHCl_3$ < *iso*butyl alcohol (**II**). To detect VO_3^-, extract the soln. with a 0·3% soln. of 8-hydroxyquinoline (**III**) in **II**. The optimum pH is 3·8 to 4·5. In the presence of NaF, V can be detected in the simultaneous presence of Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Co^{2+} and Ni^{2+}. Analogous results are obtained for the reaction product of **III** with vanadyl sulphate. To determine V in steel and cast iron, dissolve 0·5 g with slight warming in HCl (1:2)(10 ml), treat the soln. with conc. HNO_3, evaporate for 10 min. and dilute with water to 25 ml. To 5 ml add NaOH soln. dropwise to the formation of a $Fe(OH)_3$ ppt., which is dissolved in one or two drops of HCl. Then add NaF (0·7 g), a buffer soln. of pH 3·91 (10 ml) and **II** (2 ml) and extract the V by shaking for 1 min. with a 0·3% soln. of **III** in **II**. Compare the intensity of the colour with that of standard soln. C. D. KOPKIN

2599. **Spectrographic determination of small amounts of niobium in ores and refining products.** V. V. Nedler (Nigrizoloto Inst.). *Zavod. Lab.*, 1957, **23** (11), 1336–1337.—Samples are decomposed with HF and H_2SO_4 and Nb is pptd. from the soln. by means of tannin, with $SnCl_2$ added as a collector. The ignited oxides mixed with powdered quartz containing ThO_2 as internal standard are subjected to arc excitation, and the lines Nb 3163·40 - Th 3154·73 A (with niobium contents between 0·02 and 0·4%) or Nb 2927·81 - Th 2942·86 A (with niobium contents between 0·08 and 1·0%) are measured. G. S. SMITH

2600. **Analysis of pure metals. Determination of tantalum impurities in zirconium and niobium.** V. A. Nazarenko and M. B. Shustova. *Zavod. Lab.*, 1957, **23** (11), 1283–1286.—Derivatives of 2:3:7-trihydroxy-6-fluorone, particularly the 9-(*p*-dimethylaminophenyl) derivative (**I**), are sensitive colour reagents for Ta. A reagent soln. of **I** is prepared by mixing 50 mg with 0·5 ml of $6\ N$ HCl, adding 50 ml of ethanol, filtering, washing the filter with ethanol and diluting the filtrate to 100 ml. With Ta in slightly acid soln. the reagent gives a bright red ppt. or a colloidal soln. which may be stabilised with gelatin. In 10 ml of soln. $0{\cdot}1\ N$ in HCl and containing 0·4% of ammonium oxalate and 1 ml of 1% gelatin soln. the minimum amount of Ta detectable is 3 μg. No interference is caused by 400 μg of Nb (in presence of the oxalate), 100 μg of Ti, 500 μg of Zr, 150 μg of W, 100 μg of Mo, 500 μg of Sb^{3+}, 3 μg of Sb^{5+}, 5 μg of Sn^{4+}, 3 μg of Ge or 1000 μg of Fe, if H_2O_2 is added. The max. absorption of **I** occurs at 470 mμ and that of the tantalum complex at 500 mμ, but a photometer with a 530-mμ filter is suitable for the determination of Ta. *Zirconium*—The sample (1 g) is decomposed with HF and the residue obtained after evaporation to dryness is dissolved in 20 ml of an acid mixture obtained by diluting 70 ml of $11\ N$ HNO_3 with 118 ml of water and adding slowly 12 ml of 40% HF. After extraction with acetone - *iso*butyl alcohol (2 × 10 ml) in the presence of

10 ml of a saturated soln. of $(NH_4)_2SO_4$, the combined extract is treated twice with 15-ml portions of a wash soln. [prepared by shaking 30 ml of a mixture of 70 ml of 11 *N* HNO_3, 106 ml of water and 24 ml of 40% HF with 20 ml of saturated $(NH_4)_2SO_4$ soln., 20 ml of acetone and 20 ml of *iso*butyl alcohol, and collecting the lower layer]. The extract containing the Ta is evaporated with 10 ml of 5% boric acid soln. and 1 ml of conc. H_2SO_4, and the residue is fused with 0·5 g of $K_2S_2O_7$. The melt is dissolved in 5 ml of 4% ammonium oxalate soln. and the diluted soln. is mixed with 2 drops of 2:4-dinitrophenol soln. (0·2% in *N* KOH) and 2·5 ml of 2 *N* HCl and diluted to 50 ml. An aliquot (10 to 20 ml) is mixed with 1 ml of gelatin soln. and 1 ml of the reagent soln. and diluted to 25 ml with a diluting soln. (prepared by dissolving a cooled melt of 10 g of $K_2S_2O_7$ in 100 ml of 4% ammonium oxalate soln., adding 250 ml of water, neutralising to 2:4-dinitrophenol with *N* KOH, adding 50 ml of 2 *N* HCl and diluting to 1 litre). The soln. is then treated as described in the procedure for obtaining a calibration curve. *Standardisation*—A soln. of Ta (500 μg in 5 ml) is evaporated to dryness and the residue is ignited and fused with 1 g of $K_2S_2O_7$. The melt is dissolved in 10 ml of 4% ammonium oxalate soln., the soln. is neutralised to 2:4-dinitrophenol with *N* KOH, 5 ml of 2 *N* HCl is added, and the soln. is diluted to 100 ml. Aliquots (1 to 10 ml) are placed in 25-ml calibrated flasks and to each flask, together with a blank, are added 10 ml of the diluting soln. (see above), 1 ml of 1% gelatin soln. and 1 ml of the reagent soln. The soln. are heated (100°) for 5 min. and set aside for 3 hr. After addition of 1 ml of 3% H_2O_2 the soln. are diluted to the mark with the diluting soln. and the extinction is measured after 10 min. From the results a calibration curve is drawn. *Niobium*—The sample (0·2 to 1 g) is dissolved in conc. HF and HNO_3, the residue after evaporation to dryness is dissolved in 15 ml of the acid mixture used with Zr, and the soln. is extracted similarly. The pyrosulphate melt obtained from the material extracted is dissolved in 10 ml of 40% oxalic acid soln., the soln. is neutralised with *N* KOH, 5 ml of 2 *N* HCl is added and the soln. is diluted to 100 ml with water. The soln. at 50° to 60° is treated with 25 to 50 ml of the reagent soln. to precipitate Ta, which is not completely removed by the extraction process. The ppt. is filtered off after 12 hr. and washed with the diluting soln. with the addition of some **I**. The ppt. is ignited, the ash is treated with 1 ml of HF and a few ml of conc. H_2SO_4 and fused with 0·5 g of $K_2S_2O_7$, the melt is dissolved in ammonium oxalate soln., and the soln. is treated as described for Zr. With a sample wt. of 1 g, 0·002% of Ta in zirconium or niobium can be determined. G. S. SMITH

2601. **Separation of protactinium from thorium with a cation-exchange resin.** Kenjiro Kimura, Yuji Yokoyama, Hirotoshi Sano and Hisao Mabuchi (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *Japan Analyst*, 1957, **6** (10), 637–641.—Protactinium-234*m* (half-life 1·18 min.), the decay product of ^{234}Th, is quant. eluted from a column of Dowex-50X-12 resin (100 to 150 mesh, section 1 sq. cm, length 1·5 cm) with 0·8 to 2·0 *N* HNO_3 or 0·05 to 0·7% oxalic acid (rate of flow 5 ml per min.) (15 ml). The K_d value of Pa is < 3 in $> 1{\cdot}0$ *N* HNO_3, and < 1 in $> 0{\cdot}2\%$ oxalic acid. This method is satisfactorily used for the carrier-free separation of Pa. A sample of $UO_2(NO_3)_2$ (500 g) is dissolved in 2 *N* HNO_3 and treated with $La(NO_3)_3$ (50 mg) and HF to precipitate LaF_3 and ThF_4. The ppt. is dissolved in *N* HNO_3 and made ammoniacal to precipitate the hydroxides. The ppt. is washed thoroughly, then dissolved in dil. HNO_3 and added to the column, which is washed with 2 *N* HNO_3 to remove the last trace of U and eluted with 0·5 *M* oxalic acid to collect carrier-free ^{234}Th; La remains on the column (Johansson, *Svensk Kem. Tidskr.*, 1953, **65**, 79). The eluate is evaporated to dryness, heated to remove oxalic acid and dissolved in *N* HNO_3. The product is passed through the resin column, which is eluted with 2 *N* HNO_3 to collect Pa. The Th adsorbed on the resin can be eluted with > 3 *N* HNO_3. K. SAITO

2602. **Apparatus for analysis of mixtures of oxygen, nitrogen and argon.** L. I. Kazarnovskaya, N. M. Dykhno and G. B. Narinskiĭ (All-Union Sci. Res. Inst. of Oxygen Engng). *Zavod. Lab.*, 1957, **23** (11), 1387–1388.—Heated tubes containing Cu and Ca are used for absorptions, and pressure measurements are made from which the gas composition can be determined. G. S. SMITH

2603. **Rapid determination of sulphur in iron and manganese ore by a combustion method followed by EDTA titration.** Yoshihide Endo and Masaharu Iwata (Fukiai Plant, Kawasaki Steel Ind., Wakihama-cho, Fukiai-ku, Kobe). *Japan Analyst*, 1957, **6** (9), 586–587.—The SO_2 liberated by combustion at 1350° to 1400° (in a tube normally used for the analysis of iron and steel) is absorbed in 0·1% H_2O_2 (30 ml), titrated with 0·02 *N* NaOH (to methyl red) and boiled with a known small excess of 0·01 *M* $BaCl_2$ (calculated from the titration with NaOH) for 2 min. The product is cooled, mixed with 0·01 *M* $MgCl_2$ (1 ml), buffer soln. (8·25 g of NH_4Cl and 113 ml of aq. NH_3 soln. per litre) (10 ml), KCN (5%, 3 drops) and Eriochrome black T (0·1% in methanol) and titrated with 0·01 *M* EDTA. The results compare favourably with those by other methods. K. SAITO

2604. **Determination of sulphur in various materials [coal, ores, etc.] by reduction with zinc vapour.** M. S. Kurchatov (Chem. Inst., Bulgarian Acad. Sci.). *Zavod. Lab.*, 1957, **23** (11), 1294–1296.—The finely ground sample containing $\simeq 3$ to 5 mg of S is mixed with 0·5 g of Eschka's mixture in a porcelain crucible; a piece of zinc (0·5 to 0·8 g) is added, followed by a layer of Eschka's mixture. If the sample contains polysulphides, As, Sb, Pb, Mg or elementary S, the sample is first mixed with 0·5 g of zinc powder and a few crystals of $SnCl_2$. The crucible is covered with a close-fitting lid held by a clamp and heated at 920° to 950° until zinc vapour ceases to come off. The crucible is transferred to a flask and the sulphides are decomposed in a stream of H_2S-free CO_2 with HCl. The H_2S is absorbed in a 5% soln. of Cd acetate in 25% acetic acid, and the CdS is determined iodimetrically. G. S. SMITH

2605. **Determination of sulphur in glass.** J. P. Williams, F. J. Farncomb and T. S. Magliocca (Corning Glass Works, New York). *J. Amer. Ceram. Soc.*, 1957, **40** (10), 352–354.—The total S (0·01 to 1%) was determined by combustion in O (with Sn and Fe as accelerators and with MgO if As was present) at 1650° in an induction-heated tubular Leco Furnace No. 5215, the SO_2 being automatically titrated with a Leco Titrator E.T.20. The results agreed well with those by wet chemical analysis. The sulphide S was determined by pptn.

as Ag_2S. *Procedure*—The sample (0·3 g) is digested in a platinum vessel on a steam bath for 30 min. with 40 ml of 1% Ag acetate soln. and 40 ml of 48% HF. The soln. is filtered (plastic or wax-protected glass), and the ppt. is washed thrice with 5% HF and 10 times with H_2O (and 5 times with 5% aq. NH_3 soln. if AgCl is present). The ppt. is ignited with 5 ml each of 36 *N* H_2SO_4 and 12 *N* HNO_3, fumed with H_2SO_4, cooled, diluted to 200 ml and titrated potentiometrically with 0·02 *N* NH_4SCN, a valve voltmeter or pH meter and a silver - silver chloride/gold electrode system being used.

J. A. SUGDEN

2606. **[Colorimetric reagent for the] detection of sulphur dioxide.** Mine Safety Appliances Co. [Inventor: P. W. McConnaughey]. Brit. Pat. 793,727; date appl. 5.12.55.—The reagent is the blue reaction product of tetramethyldiaminodiphenylmethane and a dil. solution of I, Br or HNO_3 carried on an inert granular solid, *e.g.*, silica gel.

J. M. JACOBS

2607. **Rapid determination of selenite with potassium ferricyanide.** F. Solymosi (Inst. for Inorg. and Anal. Chem., Sci. Univ., Szeged, Hungary). *Magyar Kém. Foly.*, 1957, **63** (11), 313–316.—The oxidation of SeO_3^{2-} by $Fe(CN)_6^{3-}$ is very slow even at high temp. and high alkalinity, but it is catalysed by OsO_4. *Procedure*—Add NaOH soln. to SeO_3^{2-} (30 to 150 mg) to give 20 to 30 ml of a 3·5 to 5 *N* NaOH soln. Heat to between 55° and 65°, add 0·01 *M* OsO_4 (3 drops) and titrate with 0·1 *M* $K_3Fe(CN)_6$. The end-point can be detected by the dead-stop method, with a sensitive ammeter (10^{-6} to 10^{-8} amp. per division) or potentiometrically. The temp. must not fall below 40° or the alkalinity below 2·5 *N*. If KOH is used, the initial alkalinity can be 2 to 3 *N*. The error is 0·15 to 0·2%. Ions that have a low redox potential interfere by reducing the $Fe(CN)_6^{3-}$. Tellurite and tellurate interfere by forming a complex with OsO_4; NH_3 behaves similarly and must be boiled out of the alkaline soln. if its concn. is > 0·02 *N*. The dead-stop method cannot be used in the presence of Hg^{2+} or Tl^{3+}.

A. G. PETO

2608. **Micro-determination of chromium with 1:5-diphenylcarbohydrazide [*sym.*-diphenylcarbazide].** T. L. Allen (Univ., Davis, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 447–450.—The influence of operational variables on the colorimetric micro-determination of Cr^{VI} with *sym.*-diphenylcarbazide (**I**) has been studied. Most critical are the quality of solid **I** and of the stock soln. used; other variables (pH, temp., concn., order of mixing, ionic strength) can be safely changed within quite wide limits. Pure cryst. **I** is preferred; its m.p. is 9° above that of the phenylsemicarbazide. There is complete decomposition of Na_2O_2 (0·22 g per 50 ml of H_2O) when this is used to oxidise Cr^{III} to Cr^{VI}, the recovery of Cr being ≃ 99·2%. For fresh soln. of pure **I**, the mean mol. extinction coeff. at 546 mμ is (4·17 ± 0·04) × 10^4 (21 analyses), which agrees with values in the literature.

W. J. BAKER

2609. **Photometric determination of chromium in electronic nickel.** C. L. Luke (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 359–361.—From 0·001 to 0·02% of Cr in nickel can be determined accurately by the procedure described. The sample (0·5 g) is dissolved in hot HNO_3 (1 + 1) and, if W is absent, 48% HF (1 drop); any tungstic acid is filtered off and any Cu in the filtrate is removed by a dithizone - $CHCl_3$ extraction. The Cr is then oxidised to Cr^{VI} and, after conversion of Ni and Co into perchlorates, aq. NH_3 is added to precipitate Fe, Ti and Al (together with Ni and Co as insol. NH_4ClO_4 salts). The Cr in the filtrate is determined photometrically at 540 mμ (5 cm cell) as the diphenylcarbazide complex, with H_2O as reference soln. Loss of Cr by occlusion in tungstic acid is negligible.

W. J. BAKER

2610. **Distribution of the chloride complex of molybdenum in a hydrochloric acid - organic solvent system.** F. G. Zharovskiĭ. *Zhur. Neorg. Khim.*, 1957, **2** (3), 623–627; *Ref. Zhur., Khim.*, 1957, Abstr. No. 66,363.—Thirteen oxygen-containing organic solvents are studied. On increasing the concn. of HCl the solubility of water in *n*-butanol, *iso*butyl alcohol, *iso*amyl alcohol and butyl formate increases; in *n*-butanol and *iso*butyl alcohol an equal volume of water dissolves at a concn. of HCl ≮ 5 *N*, and in butyl formate at a concn. of HCl ≮ 7 *N*. With ethyl, *iso*propyl, *iso*butyl and *iso*amyl benzoates and with ethyl and *iso*amyl salicylates there is no change of volume of the aq. and organic phases. The influence of the concn. of HCl on the distribution of the chloride complex of Mo in the HCl - organic solvent system is studied. Best results are obtained with ethyl benzoate. It is shown that with these esters the extractability of the chloride complex increases with increase of concn. of HCl. The composition of the complex, which may be extracted with diethyl ether, corresponds to $H[MoO_2Cl_3]$. It is established that addition of NH_4Cl or H_3PO_4 lowers the extractability of the complex by diethyl ether. Partial replacement of the HCl by an equivalent quantity of $CaCl_2$ or $AlCl_3$ does not influence the extractability.

C. D. KOPKIN

2611. **Photometric determination of molybdenum (V) as the thiocyanate complex.** F. Bermejo Martínez and A. Prieto Bouza (Univ. of Santiago de Compostela, Spain). *Chemist Analyst*, 1957, **46** (3), 66–67.—Interference by Cr, V and Co is avoided by forming unextractable complexes with EDTA, and interference due to Ti is prevented by adding F^-. The molybdenum - thiocyanate complex is extracted with *iso*amyl alcohol - CCl_4. Molybdenum has been determined in soils dissolved in H_2SO_4 and HF, in plant materials dissolved in HNO_3 and $HClO_4$, and in ferrous alloys dissolved in HCl and $KClO_4$, though Na_2HPO_4 is added if the concn. of W is > 1%. Details are given of reagent preparation and of the method. The colour of the complex extracted by the *iso*amyl alcohol - CCl_4 is measured at 465 mμ.

R. L. MORTLOCK

2612. ***p*-Cresotic acid—a micro reagent for uranium.** B. R. Sant and M. K. Joshi (Hindu Univ., Benares). *Naturwissenschaften*, 1957, **44** (20), 536 (in English).—A 2% soln. of *p*-cresotic acid (6-hydroxy-*m*-toluic acid) in 80% (v/v) ethanol is a sensitive reagent for U. A bright-red colour is produced in the cold, and the reaction is sensitive down to a dilution of 1 in 2 × 10^3. Free acids, Fe^{III}, Ce^{IV}, Th, phosphate, oxalate, tungstate and high concn. of Cu, Co, Ni and SO_4^{2-} interfere with the reaction. In dilute soln. the colour formed is directly proportional to the U present, and the use of this reagent for the colorimetric determination of the metal is suggested.

E. KAWERAU

2613. **Precipitation of uranium with cacodylic acid.** R. Pietsch (Inst. für anorg. und anal. Chem., Univ., Graz, Austria). *Z. anal. Chem.*, 1957, **159** (1), 37–41.—Uranium is separated quant. as its cacodylate at pH 4 to 7 by the addition of a 25% soln. of crystalline Na cacodylate to a soln. of U adjusted to the correct pH with aq. NH_3 and bromophenol blue. The ppt. may be ignited to U_3O_8, but it is preferable to dry it at 200° in a G4 sintered crucible. The conversion factor for U is then 0·4376. Chloride and NO_3^- do not interfere. Tartrate must be absent, whilst acetate will interfere at pH 4 but not at pH 6 to 7 if present in a moderate excess. Similarly SO_4^{2-} will interfere at pH 4, but even a large excess can be tolerated at pH 6 to 7. J. H. WATON

2614. **Determination of small quantities of uranium by the fluorescence method.** V. A. Unkovskaya. *Trudy Radiev. Inst., Akad. Nauk, SSSR*, 1957, **5** (2), 117–128; *Ref. Zhur., Khim.*, 1957, Abstr. No. 66,412.—It is established that it is possible to use this method for the determination of U in water with a very small U content, and for the estimation of approx. U content of large amounts of material. C. D. KOPKIN

2615. **Polarographic determination of uranium.** I. E. Starik and A. S. Starik-Smagina. *Trudy Radiev. Inst., Akad. Nauk, SSSR*, 1957, **5** (2), 105–116; *Ref. Zhur., Khim.*, 1957, Abstr. No. 66,411.—The conditions for the polarographic determination of U are studied and methods are described for the determination of U in certain materials (natural water, petroleum ash). No interference to the determination is caused by alkali metals, Pb, Al (0·5 to 2 *N*) or H_3PO_4 (1000 times the quantity of U). The presence of V does not influence the height of the wave due to U when the content of V in the material is considerably less than that of U (10 times less); equal or larger amounts of V interfere.

C. D. KOPKIN

2616. **Spectrochemical determination of small amounts of uranium in natural samples.** T. M. Moroshkina, V. K. Prokof'ev and M. N. Smirnova (Leningrad State Univ.). *Zavod. Lab.*, 1957, **23** (11), 1324–1327.—An a.c. arc with Mo or W, introduced into the sample as ammonium molybdate or tungstate, as internal standard, is used and the lines U II 4090·135 - Mo I 4084·393 or U II 4472·335 - W I 4484·190 A are measured. G. S. SMITH

2617. **Determination of uranium in solution by X-ray spectrometry.** H. M. Wilson and G. V. Wheeler (Phillips Petroleum Co., Atomic Energy Div., Idaho Falls, U.S.A.). *Appl. Spectroscopy*, 1957, **11** (3), 128–131.—*Cf. U.S. Atomic Energy Comm.*, Rep. IDO–14393, 1957 (*Anal. Abstr.*, 1958, **5**, 1188). P. T. BEALE

2618. **Spectrophotometric determination of uranium in organic-solvent solutions.** Z. I. Dizdar and I. D. Obrenović (Lab. of Phys. Chem., Inst. of Nuclear Sciences "Boris Kidrich," Belgrade, Yugoslavia). *Analyst*, 1958, **83**, 177–179.—The method is a combination of two procedures, *viz*, extraction of the U from the organic phase with a complexing agent and development of a colour in the aq. phase with the same complexing agent for the spectrophotometric determination. This avoids the search for a reagent that would form a homogeneous phase with many different organic solvents. The ammonium thioglycollate reagent of Davenport *et al.* (*Brit. Abstr. C*, 1950, 87) was found to be suitable. To an aliquot of the organic soln. are added 2 ml of dil. aq. NH_3 (1 + 1) and 2 ml of the thioglycollate reagent (10 ml of thioglycollic acid diluted with water, neutralised with aq. NH_3 and diluted to 100 ml). After shaking and separation of the phases, the aq. layer is diluted to 25 ml, the organic layer is removed and the aq. layer is examined spectrophotometrically. The method was applied to soln. of U in tri-*n*-butyl phosphate, *iso*butyl methyl ketone, ethyl acetate and diethyl ether. The use of tri-*n*-butyl phosphate was examined in detail and in the presence of different diluents, *viz*, kerosine, diethyl ether, diisopropyl ether, hexane and CCl_4, and the results are tabulated.

A. O. JONES

2619. **Automatic determination of uranium in process streams.** H. W. Bertram, M. W. Lerner, G. J. Petretic, E. S. Roszkowski and C. J. Rodden (U.S. Atomic Energy Commission, New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 354–359.—From 100 to 200 g of U per litre of feed solution can be determined continuously, at 5-min. intervals, in the apparatus described and illustrated. It comprises a sampler and rotary-valve proportioner, whereby the O-free sample is diluted to $\simeq$ 1 in 400 and mixed with the supporting electrolyte (0·1 *M* H_2SO_4 - 0·1 *M* Na_2SO_4), and a derivative polarograph in which $E_{\frac{1}{2}}$ for UO_2^{2+} is measured at 25° with a mercury-pool electrode. The derivative polarograph is based on a resistance - capacitance circuit, and scans the applied voltage in the reverse direction to decrease peak oscillations. Specific calibration curves for each type of feed are advisable. The precision of the method is 0·5% and the max. error is $\pm$ 5·5% (generally positive). Vanadium and Mo interfere; separate calibration curves are recommended for V-rich feeds.

W. J. BAKER

2620. **Volumetric determination of uranium in presence of iron.** M. W. Desai and T. K. S. Murthy (Chem. Div., Atomic Energy Estab., Trombay, Bombay, India). *Analyst*, 1958, **83**, 126–129.—The soln. of uranium sulphate ($\equiv \simeq$ 100 mg of U_3O_8) is acidified with conc. H_2SO_4 (2·5 ml) and diluted to 50 ml. When cold it is passed through a Jones reductor which is then washed with 5% w/v H_2SO_4. Clean air is bubbled through the reduced soln. to oxidise any U^{III}, a known amount of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln. (0·05 *N*) is added and after 5 min. the residual Fe^{III} is determined by addition of KI and osmium tetroxide soln. (as catalyst) and titration of the liberated iodine with $Na_2S_2O_3$ soln. The presence of PO_4^{3-} (up to the equiv. of 500 mg of P_2O_5) does not cause interference. Owing to the mild oxidising power of $(NH_4)_2SO_4.Fe_2(SO_4)_3$, the method is not affected by the presence of appreciable amounts of NO_3^-.

A. O. JONES

2621. **Determination of uranium in rocks and minerals by fluorescence.** I. E. Starik, L. Ya. Atrashenok and A. Ya. Krylov. *Geokhimiya*, 1956, (8), 39–46; *Ref. Zhur., Khim.*, 1957, Abstr. No. 66,414.—Fuse the sample of rock with a known quantity of NaF, then remove the melt completely from the crucible and grind it in an agate mortar. Prepare 3 or 5 beads of wt. about 5 mg and measure the intensity of the luminescence, with $n \times 10^{-9}$ to $n \times 10^{-8}$ g of U in each bead. The accuracy of

the measurements is ± 20%. The influence of separate elements on the luminescence of U in NaF depends on the character of the element and its concn. in the bead. For each element there exists a limiting concn. in the NaF at which its presence does not affect the intensity of the luminescence. For artificial mixtures of composition close to that of rocks and minerals, the degree of dilution necessary to exclude the influence of admixtures of other elements is established. The minimum amount of U which can be determined is at dilutions of $n \times 10^{-5}$ g per g of rock or mineral. The minimum dilution necessary is established by gradually increasing the ratio of sample to NaF until the influence of the impurities disappears. For quartz and dolomite the necessary dilution in the flux is 1:20, for felspar and calcite 1:80, for biotite 1:200, for wolframite 1:2000, and so on. For minerals containing 1% or more of U, the dilution is carried out either by gradually adding further portions of NaF to the melt, or by dissolving the mineral in HCl, evaporating to dryness and dissolving the residue in N Na_2CO_3; from the basic soln. more dilute soln. are prepared. Introduce U into the beads by dipping the NaF beads in these soln. This method is not suitable for minerals of the niobite-tantalite group. The ratio of NaF to other fluxes, at which the intensity of the U luminescence is unaltered, is established. These ratios are, for $Na_2B_4O_7$, 20:1, for Na_2CO_3, 1:10, for K_2CO_3, 3:1, and for $K_2S_2O_7$, 3:1. C. D. KOPKIN

2622. **X-ray spectrometric method for determination of plutonium in solution.** D. S. Flikkema and R. V. Schablaske (Argonne Nat. Lab., Lemont, Ill.). *U.S. Atomic Energy Comm.*, Rep. ANL–5804, 1957, 11 pp.—Since this method is not affected by variations in isotopic content as is the widely used radiochemical assay, it is recommended for Pu, especially as K and L X-ray emission is not measureably influenced by the valency state of the emitting atom or ion. The method is applied to Pu in the concn. range 2 to 8×10^{-3} M with coeff. of variation ± 1·5% and ± 0·6% at the limits of this concn. range for total counting times of < 11 min. The Pu may be first separated by carrier pptn., adsorption-elution or solvent extraction, or, when the constituents are known, a calibration curve may be constructed. N. E.

2623. **Mercurimetric titrations with redox indicators. I. The determination of halides and mercuric ions, respectively.** J. Bognár and O. Jellinek (Tech. Univ. for the Heavy Industries, Miskolc, Hungary). *Magyar Kém. Foly.*, 1957, **63** (11), 309–313.—The oxidation potential of the ferricyanide ion is greatly increased even by small amounts of Hg^{2+}. By adding one drop of $K_3Fe(CN)_6$ soln., the colour change of the redox indicators at the end-point becomes very sharp. Triarylmethane indicators, even in strongly acid soln., are particularly suitable. For the titration of Cl^-, Astral blue G is recommended; for the determination of Br^-, many indicators are described. Only higher concn. of Cu, Co, Ni and Cr interfere. The titrations can be carried out in 0·1 to 0·01 N soln.; for I^-, with diphenylaminesulphonic acid as indicator, only 0·01 N concn. can be used, otherwise HgI_2 is precipitated. A. G. PETO

2624. **Photometric determination of fluorides.** J. Čelechovský and J. Holer (Pharm. Fac., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (11), 2129–2131.—The purple-red complex of phenazone with Fe^{3+} is decolorised in the presence of fluorides. *Procedure*—Dilute the neutral soln. of fluoride with dil. HNO_3 (pH 2·0) and add 0·2 M phenazone (5 ml) and, according to the thickness of the measuring cell, the corresponding amount of the soln. of $Fe(NO_3)_3$ ($10{\cdot}75 \times 10^{-6}$ mol of Fe per 25 ml for 1 cm, $5{\cdot}70 \times 10^{-6}$ mol per 25 ml for 2 cm, $3{\cdot}15 \times 10^{-6}$ mole per 25 ml for 5 cm) and compare with a blank. Strong reducing agents and compounds that form complexes with Fe^{3+} or F^- interfere; in their presence the F^- must first be separated by distillation. An excess of Cl^- or SO_4^{2-} does not interfere. J. ZÝKA

2625. **Measurement of small quantities of fluoride with the help of fluorine-18.** J. H. Fremlin, J. L. Hardwick and J. Suthers (Dept. Dental Surgery, Univ. Birmingham, England). *Nature*, 1957, **180**, 1179–1181.—An isotope-dilution method of determining microgram amounts of F^- in samples of tooth enamel (≃ 1 mg) and aq. soln. (≃ 1 ml) is based on the adsorption of F^- from acid soln. by glass. The sample soln. is mixed with a small known amount (≃ 10 μC) of almost carrier-free ^{18}F (as fluoride), and N HNO_3 is added until the pH is ≃ 2. The mixture is then applied to an area of ≃ 1 sq. cm on a clean glass slide. After ≃ 5 min. the active soln. is removed in a fast stream of H_2O (pH ≃ 6) and the ^{18}F in the glass is measured with a Geiger counter or by autoradiography followed by microphotometry. The higher the concn. of ^{19}F in the sample soln. the less the radioactivity in the adsorbed layer. A calibration curve should be prepared from results for standard soln. of F^- containing exactly the same concn. of ^{19}F and having the same pH. At the lower concn. (0·01 to 10 p.p.m.) the sensitivity is ≃ 0·0002 μg of F^- per 1 mg of sample (microphotometric readings). The method is valid for samples in lactic acid-lactate buffer at pH 4·6. Sources of error are discussed. W. J. BAKER

2626. **Detection of traces of chloride in fine chemicals.** F. Feigl, D. Goldstein and R. A. Rosell (Lab. da Produção Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Z. anal. Chem.*, 1957, **158** (6), 421–427.—Heat the sample (5 to 100 mg) with a saturated soln. of K_2CrO_4 in conc. H_2SO_4 (4 drops) on a bath of boiling water and allow the vapours to come into contact with filter-paper previously soaked in a soln. of 4:4′-bisdimethylaminothiobenzophenone. The paper turns blue in the presence of ≮ 0·2 μg of Cl^-. A blue colour is also given by Br^- or I^- and a red or blue colour by NO_2^- or NO_3^-. The method may be used to detect AgCl in the presence of silver cyanide, thiocyanate, ferrocyanide or ferricyanide. A. R. ROGERS

2627. **Data for hydrazinometric measurements. [Titration of bromate.] (Preliminary communication.)** L. Szekeres, L. G. Molnár and M. Nagy (Univ. for Agric. Sci., Budapest). *Magyar Kém. Foly.*, 1957, **63** (10), 294–295.—Bromate ions can be titrated with hydrazine sulphate in the presence of Br^- in HCl medium. The indicator is alkaline iodine soln. (1 drop) and starch soln. (1 ml). The accuracy is excellent. A. G. PETO

2628. **Iodimetric studies. IV. The determination of iodide ions in the presence of bromide ions.** L. Szekeres (Univ. for Agric. Sci., Budapest, Hungary). *Magyar Kém. Foly.*, 1957, **63** (11), 320–321.—The halides present are oxidised by treatment with chlorine water, and the soln. is made alkaline with

$NaHCO_3$; Br^- and Cl^- form hypohalites, and I^- an iodate. The hypohalites are reduced to the halides with H_2O_2 or Na oxalate (**I**), but IO_3^- remain unchanged and can be determined iodimetrically. *Procedure*—Dilute an approx. 0·1 to 0·01 *N* soln. (10 ml) containing I^-, Br^- and Cl^- with H_2O (15 to 20 ml), 0·25 *N* NaOCl (30 to 40 ml) and 10 *N* HCl (3 to 4 ml). Cautiously add $NaHCO_3$ (5 to 6 g) and then 3% H_2O_2 soln. (15 to 20 ml), and heat on a water bath for 10 to 15 min. After cooling, add H_2O (50 ml), conc. HCl (12 to 15 ml) and KI (1 g), and titrate the iodine with 0·1 *N* $Na_2S_2O_3$. Instead of H_2O_2, a 0·2 *N* soln. of **I** can be used, but if the halide concn. is $< 0{\cdot}1$ *N*, the values are then 1 to 2% high. A. G. PETO

2629. **Iodimetric studies. III. The simultaneous determination of iodate and periodate ions.** L. Szekeres (Univ. of Agric. Sci., Budapest, Hungary). *Magyar Kém. Foly.*, 1957, **63** (10), 273–275.—In a $NaHCO_3$ medium, IO_4^- are reduced to IO_3^- by means of H_2O_2. Thus in a soln. containing IO_3^- and IO_4^-, the two ions are titrated simultaneously; then the IO_4^- is reduced to IO_3^- and the total IO_3^- concn. is determined. From these data, the concn. of each ion can be calculated. *Procedure*—To $\simeq$ 10 ml of an IO_3^- - IO_4^- soln. ($\equiv$ 0·1 *N*) add KI and HCl and titrate with 0·1 *N* $Na_2S_2O_3$, consuming *x* ml. To another 10 ml of the unknown soln. add H_2O (10 to 20 ml), $NaHCO_3$ (1 to 2 g) and 3% H_2O_2 (15 ml). Heat the soln. on a water bath for 10 to 15 min., then cool it and add H_2O (20 ml), KI (1 g) and conc. HCl (5 to 10 ml). Titrate with 0·1 *N* $Na_2S_2O_3$; the consumption is *y* ml. From these, $x - y = a$, $4a = b$, and $x - b = c$, where *b* is the vol. of $Na_2S_2O_3$ soln. consumed by the IO_4^- and *c* that by the IO_3^-. The method is still accurate with a 5-fold excess of either ion. A. G. PETO

2630. **Fusion test for iron(III) employing salicylaldoxime.** J. de Oliveira Meditsch (Escola de Engenharia, P. Alegre, Brazil). *Chemist Analyst*, 1957, **46** (3), 69.—Mix a small sample with about 0·1 g of salicylaldoxime (m.p. 57°) in a micro-crucible, heat to 100° in a water bath, then cool; Fe^{3+} are detected by a violet colour. The sensitivity is 0·5 μg. A violet coloration is given with chloride, sulphate, nitrate and $K_2SO_4.Fe_2(SO_4)_3$; an orange coloration with ammonium molybdate; a red coloration with uranyl nitrate, ceric ammonium nitrate and $Bi(NO_3)_3$; and green with $NiSO_4$. Salts of Co^{II}, Cu^{II}, Cr^{III}, Mn^{II}, Sn^{II}, Pb^{II}, Al^{III}, Hg^{II}, Zn^{II} and Sb^{III}, and TiO_2, Na_2WO_4, OsO_4 and vanadyl sulphate give a pale-brown coloration. R. L. MORTLOCK

2631. **Magnetochemical and crystallographic analysis of ferromagnetic oxides by electron diffraction.** S. Yamaguchi and T. Hori (Sci. Res. Inst., Ltd., Hongo, Tokyo, Japan). *Z. anal. Chem.*, 1957, **158** (5), 360–361.—The electron diffraction patterns of NiO, Fe_3O_4 and Al_2O_3 serve to distinguish these oxides. A. R. ROGERS

2632. **Simultaneous spectrophotometric determination of micro amounts of iron and aluminium. Extraction from a large volume of sample solution.** Kenji Motojima and Hiroshi Hashitani (Fac. of Sci. and Engng, Ritsumeikan Univ., Kita-ku, Kyoto). *Japan Analyst*, 1957, **6** (10), 642–646.—Application of the simultaneous determination of Al and Fe with 8-hydroxyquinoline in $CHCl_3$ (*Anal. Abstr.*, 1956, **3**, 1725) to the analysis of natural water was studied with reference to the solubility of $CHCl_3$ (10 ml) in the water sample ($<$ 400 ml). The extinction of the $CHCl_3$ layer containing the 8-hydroxyquinoline complexes of Al and Fe increases linearly with increasing amount of the aq. soln. from which these metals are extracted. The working curve must therefore be prepared under the same conditions. The masking action of F^- in natural water is eliminated by the addition of $BeSO_4$ (3 mg of Be for 0·5 mg of F). No interference results from other common ions in natural water. Ferrous ions are readily oxidised to ferric during the shaking with $CHCl_3$. As little as 5 μg of Fe and Al can be determined in 400 ml of sample. K. SAITO

2633. **Chelatometry. XVI. Simultaneous determination of tervalent iron and aluminium ions.** P. Wehber (Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1957, **158** (5), 321–339.—To determine Fe^{III} (5 to 60 mg) in the presence of Al (5 to 30 mg), titrate with 0·1 *M* EDTA (disodium salt) at 20° and pH 1·8 to 2·0 with either (*a*) sulphosalicylic acid or (*b*) Variamine blue B (**I**) or (*c*) the leuco base of Bindschedler's green (**II**) as indicator. To determine Al in the presence of Fe^{III}, either (*d*) add excess of EDTA, adjust to pH 5·5, boil for 1 min., cool, and titrate with 0·1 *M* $CuCl_2$ with **I** and NH_4SCN as indicator; or (*e*) add excess of EDTA, adjust to pH 5·5 and titrate with 0·1 *M* $FeCl_3$, with **II** as indicator; or (*f*) add excess of nitrilotriacetic acid, adjust to pH 5·5 and titrate with 0·1 *M* $CuCl_2$, with **I** as indicator in the presence of NaCl. Procedure (*f*) is preferred, because large amounts ($\simeq$ 1000 mg) of Mg, Ca or Ba and small amounts of Mn do not interfere. To determine Fe and Al simultaneously, suitable combinations of procedures are (*a*) and (*d*); (*b*) and (*d*) or (*f*); (*c*) and (*d*), (*e*) or (*f*). The ions Cu^{2+}, Zn^{2+}, Cd^{2+}, TiO^{2+}, Pb^{2+}, Bi^{3+}, Co^{2+} and Ni^{2+} interfere. If the amount of Al is large, it is better to determine the sum of Fe and Al chelatometrically, and the Fe by another method (such as titration with dichromate). A. R. ROGERS

2634. **A new analytical method for the determination of iron in chromium-plating solutions.** H. W. Dettner (Sievekingstr. 1, Bielefeld, Germany). *Metalloberfläche*, 1957, **11**, 12–14.—Iron can be determined in chromium-plating soln. by adjusting the diluted bath to pH 2·5, adding tiron as indicator, and titrating the soln. with EDTA (disodium salt) until the blue - green colour is discharged. CHEM. ABSTR.

2635. **Analysis of nickel alloys for oxide cathodes. V. Determination of iron.** K. Riedel (Wernerwerk für Bauelemente, Siemens u. Halske A.-G., Munich, Germany). *Z. anal. Chem.*, 1957, **159** (2), 110–112.—Traces of Fe are extracted from 6·5 *N* HCl soln. with *iso*butyl methyl ketone. After being extracted back with water, the Fe^{III} is reduced with hydroxylamine hydrochloride, and 1:10-phenanthroline soln. is added. The extinction of the Fe^{II}-phenanthroline complex is measured with filter Hg 492 mm, against that of a blank. The method gives a coeff. of variation of $\pm$ 1·5%. The organic solvent is readily purified and recovered. J. H. WATON

2636. **The determination of ferrous iron in pulverised-fuel ash and slags from pulverised-fuel-fired boilers.** P. J. Jackson (Central Electricity Authority, Leatherhead, Surrey, England). *J. Appl. Chem.*, 1957, **7** (11), 605–610.—The method of Wilson [*Bull. Geol. Surv. G.B.*, 1955, (9), 56] for the determination of FeO in silicates is modified

for application to samples of 0·05 to 0·1 g and to ensure an error of $\not> \pm 0{\cdot}05\%$ on samples containing from 1 to 10% of FeO. Dissolution of the fly-ash or slag is effected with HF, at 20° for 24 to 72 hr., in the presence of an excess of 0·1 *N* sodium metavanadate soln. The remaining vanadate is titrated with 0·01 *N* $FeSO_4$ in the presence of dil. H_2SO_4 and Ba diphenylaminesulphonate (0·3%, w/v) indicator. The content of FeO (1 to 3%) in fly-ash depends on the percentage of total Fe (4 to 20% of Fe_2O_3) and C in the ash.

W. J. BAKER

2637. **Determination of small amounts of carbon in iron by proton irradiation.** J. J. Point (Inst. Interuniv. des Sci. Nucl. Cen. de la Fac. Polytech. de Mons, Belgique). UNESCO/NS/RIC/48, 1957, 8 pp. (in French).—The well-cleaned sample and a tungsten carbide standard were irradiated with protons of $\simeq 600$ keV energy. Measurement of the radiation from the ^{13}N produced by the reaction $^{12}C(p, \gamma)^{13}N$ was started within minutes of the end of the irradiation. By using a Geiger - Müller counter a limit of detection of 20 p.p.m. was reached, but the use of two scintillation counters in coincidence to record the annihilation gamma radiation enabled it to be reduced to 4 p.p.m. The production of other activities from possible impurities is considered. G. J. HUNTER

2638. **Determination of carbides in stainless steel by electrolysis.** M. M. Shapiro (Central Sci. Res. Inst. of Ferrous Metallurgy). *Zavod. Lab.*, 1957, **23** (11), 1292–1294.—Electrolysis is carried out in a soln. containing 15% of NaCl and 2·5% of tartaric or citric acid with a copper cathode and a c.d. of 0·6 to 0·7 amp. per sq. cm at 50°. G. S. SMITH

2639. **A method of micro-spectrographic analysis [of cast iron and steel].** I. L. Mirkin and É. P. Rikman (Tulsk Mechanical Inst.). *Zavod. Lab.*, 1957, **23** (11), 1338–1341.—A rectified high-frequency spark discharge is applied to local analysis of cast iron and steel. Results of determinations of Mg, Nb, Mo, Ti, Mn, Ni and Si in and around inclusions are given. G. S. SMITH

2640. **Influence of nitriding on the results of spectrographic analysis [of steel] and a method of eliminating the observed effect.** I. A. Grikit. *Zavod. Lab.*, 1957, **23** (11), 1347–1351.—Nitriding reduces the apparent content of Cr, Si, Mn, Mo and Al and increases that of Ni. It is recommended that, with spark excitation, the second electrode should be of copper and not of carbon. Alternatively an arc should be used. G. S. SMITH

2641. **Determination of magnesium in cast-iron nodules. I. Volumetric method.** J. Bernal Nievas and L. Serrano Berges (Zaragoza Univ., Spain). *Inst. Hierro y Acero*, 1957, **10** (54), 389–395.—The sample is dissolved by treatment with HCl, followed by HNO_3 and $HClO_4$. Silica is eliminated with HF. The whole or greater part of the Fe is removed by electrolysis with a mercury cathode and a Melaven cell (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 180). Manganese is not completely removed and can be eliminated, together with any residual Fe, by treatment with ammoniacal ammonium sulphide or persulphate. Finally, the Mg is pptd. as the dimethyloxinate and determined volumetrically with $KBrO_3$.

II. Indirect colorimetric method. J. Bernal Nievas and L. Serrano Berges. *Ibid.*, 1957, **10** (54), 395–399.—The ppt. of Mg dimethyloxinate obtained as in Part I is dissolved in acetic acid and diazotised by treatment with sulphanilic acid and $NaNO_2$. The colour developed is then measured, after treatment with alkali and dilution, with a 520-mμ filter; the content of Mg is derived from a calibration curve. The effects of the pH of diazotisation, the relative amounts of sulphanilic acid and $NaNO_2$ used, and the time between diazotisation and treatment with alkali have been examined.

III. Direct colorimetric method. J. Bernal Nievas and L. Serrano Berges. *Ibid.*, 1957, **10** (54), 399–401.—The sample is dissolved, the greater part of the Fe is removed electrolytically, and the remaining Fe and Mn eliminated with ammoniacal $(NH_4)_2S_2O_8$ in the presence of ammonium salts as in Part I. The solution obtained after centrifuging is evaporated, treated with HNO_3 to remove ammonium salts and re-dissolved. The Mg is then determined colorimetrically by the addition of a soln. of Eriochrome black T and a piperidine - HCl buffer of pH 11·7, spectrophotometric measurement of the absorption at 540 mμ, and reference to a calibration curve. By this procedure, samples of 1 g with a content of Mg of $\simeq 0{\cdot}03\%$ can be analysed. L. A. O'NEILL

2642. **Spectrophotometric silicon determination in alloy steels using stannous oxalate as reductant.** M. T. Hall (67 Minshall New Road, Crewe, Cheshire, England). *Chemist Analyst*, 1957, **46** (3), 64–66.—Stable stannous oxalate, with reproducible reducing action, is used as reductant for heteropolymolybdates of Si or P in their spectrophotometric determination in steel (*cf.* Ingamells, *Ibid.*, 1956, **45**, 10). If the determination of P is unnecessary, the dissolution of the steel is best carried out with H_2SO_4, even for samples containing up to 2% of Si. The sample is warmed (but not boiled) with H_2SO_4 (1:19), $KMnO_4$ soln. is added dropwise in slight excess, then the soln. is boiled for 1 min., cleared with H_2O_2, cooled and diluted. To a portion of the soln., after dilution and addition of ammonium molybdate soln., is added H_2SO_4 (1:3). When the mixed soln. clears, stannous oxalate reagent is added, the soln. is diluted to standard vol. and after 10 min. the absorption is measured at 650 mμ against water as reference. A blank may be prepared by adding H_2SO_4 before molybdate. Calibration of the spectrophotometer with pure Si is described. R. L. MORTLOCK

2643. **Electrolytic determination of lead in iron and steel.** Hidehiro Gotô and Yachiyo Kakita (Tohoku Univ., Sendai, Japan). *Sci. Rep. Res. Inst., Tohoku Univ., A*, 1957, **9**, 131–137.—Add 5 g of sample to 70 ml of H_2O, followed by the slow addition of 70 ml of HNO_3. Heat the mixture until solution is complete and NO is expelled, then transfer the soln. to an electrolytic cell, and dilute to 750 ml with water. Electrolyse at 0·6 to 0·7 A for about 6 hr. with a platinum gauze anode and spiral cathode. Wash the electrodes with H_2O and ethanol, dry at 190° for 20 min., and weigh. Deposition of PbO_2 is complete if the total vol. is adjusted so that Fe is present in the concn. of 1 g per 150 ml of soln. Molybdenum in concn. $> 0{\cdot}1\%$ interferes with the deposition of PbO_2; Mn and Cr in amounts normally present in iron and steel do not interfere. In the concn. range 0·049 to 0·296% of Pb, the absolute deviation from the amount added to synthetic standards is $\not> 0{\cdot}003\%$. It is recommended that Pb in concn. $< 0{\cdot}01\%$ be determined by a photometric method combined with the procedure described above. CHEM. ABSTR.

2644. **Photometric semi-micro procedure for the determination of phosphorus, especially in steel and inclusions.** U. Bohnstedt and R. Budenz (Inst. für Metallforschung, Saarbrücken). *Z. anal. Chem.*, 1957, **159** (1), 12–21.—In the photometric determination of P as molybdenum blue, there is no reliable reagent for the reduction of the molybdophosphoric acid. The single-stage procedure described by Zinzadze (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 227) is recommended, in which the molybdenum blue is developed in the phosphate test soln. by the addition of a soln. containing Mo^{IV} and Mo^{VI}. The interference due to As^{V} and Si is overcome by reduction and by the use of high acidity, respectively. Iron also interferes, and is best removed by fusion with mixed alkali-metal carbonates after evaporation to dryness of the soln. of the sample in HNO_3. By this method, 5 to 120 μg of P in a 0·1-g sample may be determined. The procedure may take up to 3 days.

J. H. WATON

2645. **Photometric semi-micro determination of arsenic, especially in steel, iron and inclusions.** U. Bohnstedt and R. Budenz (Inst. für Metallforschung, Saarbrücken). *Z. anal. Chem.*, 1957, **159** (2), 95–102.—The procedure for the photometric determination of P according to Zinzadze's method with single-stage reduction (*cf. Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 227) is suitable for the determination of As. The extinction of the molybdenum blue is measured at 900 mμ. When As and P are both present, the As is separated by distillation from HCl in the presence of $FeSO_4$ and KBr. The distillate is adjusted to pH $\simeq$ 5 with $NaHCO_3$ and *N* H_2SO_4, the As^{III} is oxidised with 0·01 *N* $KMnO_4$ and the determination is completed colorimetrically after the addition of the Mo^{IV} - Mo^{VI} reagent. When the sample is solid, it is most suitably dissolved in HNO_3 - $HClO_4$ - H_2O (1:1:1). By this method, amounts of As in the range 0·03 to 0·15 mg can be determined. The time required for the analysis is 45 min. J. H. WATON

2646. **Photometric semi-micro determination of sulphur, especially in steel, iron and inclusions.** U. Bohnstedt and R. Budenz (Inst. für Metallforschung, Saarbrücken). *Z. anal. Chem.*, 1957, **159** (2), 102–109.—Sulphur is determined photometrically as the complex between formaldehyde and the reduction product of fuchsine with SO_2, described by Atkin (*Anal. Chem.*, 1950, **22**, 947). After combustion of the sample (sufficient to contain 0·005 to 0·05 mg of S), the SO_2 is absorbed in 50 ml of H_2O and 10 ml of 1% $NaHCO_3$ soln. The soln. is acidified with 5 ml of H_2SO_4 (1:3), and 1 min. later 10 ml of 0·01% fuchsine soln. is added. The soln. becomes colourless, and, after 10 min., 1 ml of formaldehyde is added. The soln. is diluted to 100 ml, and the extinction is measured at 580 mμ after a further 10 min. Care must be taken to ensure that the correct amounts of reagents are added at the correct moment. J. H. WATON

2647. **Use of amines in inorganic polarography. VI. Determination of cobalt in steel and ores.** J. Doležal and J. Novák (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1957, **51** (10), 1798–1803.—A rapid polarographic determination of Co in the presence of Fe, Al, Cr, Mn, Ni, Zn, V, Mo and W has been developed, with a mixture of *M* ethylenediamine and *M* KOH as supporting electrolyte. In this medium, Co, after having been oxidised with air, forms a complex ion $[Co(en)_3]^{3+}$, which gives a well-developed polarographic wave ($E_{\frac{1}{2}} = -0{\cdot}71$ V). *Procedure for steel*—Dissolve the sample (0·1 g) (containing about 1% of Co) in H_2SO_4 (20%) (7 ml) (or in a mixture of $HClO_4$ and HNO_3) and evaporate twice with conc. H_2SO_4. Cool the residue, add H_2SO_4 (20%) (3 ml), transfer to a 100-ml flask, add KOH (to about pH 2) and adjust the vol. with H_2O. Measure 10 ml into a 25-ml flask, add a mixture of freshly prepared 2 *M* ethylenediamine with 2 *M* KOH (12·5 ml), mix, adjust the vol. and centrifuge the ppt. Transfer the clear soln. into the polarographic vessel, bubble with air (1 min.), remove O with N and record the polarographic wave from $-0{\cdot}2$ to $-1{\cdot}2$ V, with the use of a 4-V accumulator. Evaluate the results by the use of the method of standard addition. *Procedure for ores*—Dissolve the finely powdered sample (1 g) (containing 0·1 to 1% of Co) with 10 ml of hot aqua regia. Evaporate twice to dryness with conc. HCl, dissolve the residue in conc. HCl (10 ml) and transfer the soln. (with undissolved residue) into the 100-ml flask and continue as described above. The preliminary separation of large amounts of Cu and Pb is necessary. J. ZÝKA

2648. **Differential spectrophotometric determination of cobalt.** J. de Oliveira Meditsch (Escola de Engenharia, Porto Alegre, Brazil). *Rev. Quim. Ind., Rio de Janeiro*, 1957, **26**, 185–186, 193.—The method of Bastian (*Anal. Chem.*, 1951, **23**, 580) is applied to the determination of Co in salts, with an accuracy of about $\pm$ 0·04%. From the slit aperture of 0·600 mm, the width of spectrum used at 510 mμ is only 24 mμ, so that interference from Cu^{II}, Fe^{III} and Ni^{II} in the amounts usually present in cobalt salts is negligible. The presence of Cr^{VI} leads to large errors. It is necessary that standards and samples should be subjected to the same temperature influences, and should be read alternately. G. F. PENNY

2649. **Photometric determination of cobalt as tributylammonium hexathiocyanatocobalt(II).** M. Ziegler, O. Glemser and E. Preisler (Anorg.-chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1957, **158** (5), 358–360.—The method described previously (*cf. Anal. Abstr.*, 1956, **3**, 3349) has been applied to the determination of Co in steel, alloys, pyrites, glass, zinc oxide and similar materials.

A. R. ROGERS

2650. **Quinoxaline-2:3-dithiol as a colorimetric reagent. Determination of nickel in ammoniacal solutions.** D. A. Skoog, Ming-Gon Lai and A. Furst (Univ., Stanford, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 365–368.—From 0·03 to 3 p.p.m. of Ni can be determined, to within $\simeq$ 1%, in ammoniacal soln. by measuring the extinction at 520 mμ of the pink complex of Ni with quinoxaline-2:3-dithiol. Silver, Cu, Co and Mn interfere. *Procedure*—To an almost neutral aliquot ($\equiv$ 2 to 25 μg of Ni) add conc. aq. NH_3 (10 ml) and 0·02 *M* quinoxaline-2:3-dithiol (3 ml). Dilute to 25 ml and, after $\lt$ 30 min., measure the extinction of this soln. and the blank in a Beckman spectrophotometer with 1-cm Corex cells. The concn. of Ni is read from the working curve, which is linear. Variables in and possibilities of the method are discussed. W. J. BAKER

2651. **Determination of metallic nickel in the presence of nickelous oxide.** E. Krejcar (Res. Inst. Oils, Prague). *Chem. Listy*, 1957, **51** (11), 2137.—Place the sample containing approx. 0·05 g of

metallic Ni in a flask and add a soln. of 60 g of $NH_4Fe(SO_4)_2$ in 1 litre of 0·001 *N* H_2SO_4. Heat to 60° and mix with a stream of N. When the metallic Ni is dissolved (60 to 120 min.), make the soln. up to volume with H_2O and titrate an aliquot with 0·1 *N* $K_2Cr_2O_7$. J. ZÝKA

2652. **Effect of zinc on the cyanide titration of nickel.** R. S. Young (Internat. Nickel Co. of Canada Ltd., Copper Cliff, Ontario). *Chemist Analyst*, 1957, **46** (3), 69, 75.—Zinc interferes with the cyanide titration of Ni. Citrate added before the nickel soln. is made ammoniacal produces high results if Zn is present, but substitution of $Na_4P_2O_7$ for citrate decreases interference due to Zn.
R. L. MORTLOCK

2653. **Photometric determination of small amounts of nickel in ores.** Kiyoshi Isono (Geological Survey of Japan, Hisamoto-cho, Kawasaki). *Japan Analyst*, 1957, **6** (9), 557–561.—Sandell's colorimetric determination of Ni (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 309) was applied to various ores (0·005 to 2% of Ni) with slight modifications. The unwanted pptn. of Ni dimethylglyoxime (at concn. of Ni up to 1·5 mg per 100 ml) is prevented by the addition of 25% NH_4Cl soln. (10 ml) before the addition of dimethylglyoxime (**I**). The presence of $<$ 50% of Mn (in ore), $<$ 10% of Cu, $<$ 3% of Co and $<$ 20% of Cr does not cause interference. The gravimetric determination of $<$ 0·2% of Ni in ore, especially in the presence of much Fe, is inaccurate, owing to incomplete pptn. The colorimetric method is little affected by Fe. *Procedure*—Decompose the sample (0·5 g) with HCl (20 ml) and HNO_3 (5 to 10 ml) (for oxide ores) or with HNO_3 (20 ml) and HCl (10 to 20 ml). Add H_2SO_4 (1 + 1, 10 ml), heat to white fumes, cool, dilute with H_2O ($\simeq$ 50 ml), filter, wash the ppt. with hot water, and make the filtrate up to 250 ml. Add citric acid (50%, 2 ml) to a 25-ml portion, neutralise with aq. NH_3 soln. and add 1 ml in excess. Add **I** soln. in ethanol (1%, 2 ml) and extract with 3 portions of $CHCl_3$ (5, 5, 3 ml). Extract back the Ni with two portions of 0·5 *N* HCl (10, 5 ml) and treat the aq. soln. with 25% NH_4Cl (1 ml) and saturated bromine soln. (2 ml); neutralise with aq. NH_3 soln. and then make ammoniacal. Dilute the product to 100 ml with 1% **I** in 1% NaOH soln. (2 ml) and measure the extinction at 430 mμ after 5 to 30 min.
K. SAITO

2654. **Spectrophotometric determination of nickel in copper - nickel alloys.** G. R. Sutcliffe and D. M. Peake (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1958, **83**, 122–125.—To prepare the calibration graphs, amounts of Ni ranging from 0·06 to 0·11 g, having added to each the amount of Cu necessary to make a total sample of 1 g, are dissolved in dil. HNO_3, H_3PO_4 is added and the mixture is evaporated to low bulk to remove nitrous fumes. The diluted liquid is treated with H_2O_2, boiled, cooled and diluted to 100 ml. The extinction is measured at 395 mμ, a wavelength at which only Ni absorbs, and again at 490 mμ when neither metal absorbs. The extinctions are measured with reference to a standard soln. containing 0·05 g of Ni and 0·95 g of Cu per 100 ml. This procedure applies to samples containing 5 to 11% of Ni. For other ranges the procedure is similar, and measurements are made against an appropriate reference soln. Samples of unknown composition (1 g) are treated exactly as described for the calibration graph.
A. O. J

2655. **Study of the reaction of thionalide with the platinum metals and the use of the compounds formed in analysis.** N. K. Pshenitsŷn and I. V. Prokof'eva. *Zhur. Neorg. Khim.*, 1957, **2** (3), 569–575; *Ref. Zhur., Khim.*, 1957, Abstr. No. 69,098.—The pptn. of Rh, Ir, Pd and Pt with thionalide (**I**) is studied. On adding a 1 to 2% acetic acid soln. of **I** to a soln. of sodium chlororhodate containing a small quantity of NaCl and HCl (pH 0·6), a yellow ppt. of $Rh(C_{12}H_{10}ONS)_3$ separates, which is insoluble in boiling HCl, aq. NH_3, NaOH soln. and ethanol. The presence of large amounts of HCl in the soln. hinders the pptn. For the quant. determination of Rh, remove HCl by evaporation on a boiling-water bath, dissolve the residue in water, add a soln. of **I** and boil for 30 min. The content of Rh is calculated from the wt. of the ppt. or from the wt. of metallic Rh after ignition. Sodium chloroiridate is reduced to chloroiridite and pptd. in the absence of HCl with a soln. of **I**. The yellow ppt. has the composition $Ir(C_{12}H_{10}ONS)_3$. The Ir is determined as for Rh. Palladium forms with **I** a yellow ppt. of composition close to $Pd(C_{12}H_{10}ONS)_2$. A small quantity of HCl does not interfere. In the absence of other platinum metals, Pd forms with **I** a ppt. which is soluble in benzene. Platinum forms with **I** a pale-yellow ppt. of composition close to $Pt(C_{12}H_{10}ONS)_4$; HCl interferes. The relative error in determining Rh, Ir, Pd and Pt is 1 to 3%. C. D. KOPKIN

2656. **Use of ion exchange in the analysis of the platinum metals. I. Separation of copper, nickel, iron and lead from platinum, palladium, rhodium and iridium.** N. K. Pshenitsŷn, K. A. Gladŷshevskaya and L. M. Ryakhova. *Zhur. Neorg. Khim.*, 1957, **2** (5), 1057–1068; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,370.—It is established that freshly prepared complex chlorides of Pt, Pd, Rh and Ir in the presence of Cl^- remain completely in soln. when passed through a column of Espatit KU-1. Confirmation is obtained of the lower stability of the complex anion $PdCl_4^{2-}$ as compared with $PtCl_6^{2-}$. The conditions for the quant. removal of Cu, Ni, Fe and Pb from Pt, Pd, Rh and Ir are established. The use of the ion-exchange method for removing Cu, Ni, Fe and Pb in the analysis of materials containing platinum metals shortens the time for the analysis and gives completely satisfactory results. C. D. KOPKIN

2657. **Use of chlorine in the attack of noble metals. Quantitative recovery of micro amounts of platinum, ruthenium and osmium.** A. D. Westland and F. E. Beamish (Univ., Toronto, Canada). *Anal. Chem.*, 1958, **30** (3), 414–418.—An apparatus and procedure are described whereby $<$ 2 mg each of Pt, Ru and Os in their alloys can be recovered almost quant. by dry chlorination at 700° in a silica tube. The tube (7 mm diam.) has a bulb (15 mm diam.) blown at the zone where greatest condensation of ruthenium and platinum chlorides occurs, *i.e.*, just inside the furnace at the outlet end. The hotter parts of the tube are coated with fused NaCl to ensure complete conversion of Ru into sol. chlorides and to prevent formation of insol. $PtCl_2$. The more volatile chlorides of Os are absorbed in a train of receivers containing 6 *N* HCl kept saturated with SO_2. After chlorination for several hours, the system is flushed with N, the solutions and tube washings are combined and evaporated to small vol. The Os or Ru or both are distilled and separated (*cf. Anal. Abstr.*, 1954, **1**, 1852), and then determined spectrophotometrically as the thiourea

complexes. Platinum is determined photometrically by the $SnCl_2$ method. If the concn. of Ru is high (1 to 2 mg), appreciable amounts of insol. ruthenium chlorides are formed; these can be best determined directly by distillation. W. J. BAKER

2658. **Quantitative determination of chloroplatinite in the presence of chloroiridite.** E. A. Belousov and A. A. Grinberg. *Trudy Leningr. Tekhnol. Inst. im. Lensoveta*, 1957, (40), 41–43; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,688.—The behaviour of the ion $IrCl_6^{3-}$ in aq. soln. in the potentiometric titration with $KMnO_4$ is studied. After 2 days at room temp. about 4% of the $IrCl_6^{3-}$ in a soln. of $(NH_4)_3[IrCl_6]$ ($1{\cdot}1 \times 10^{-3}$ *M*) is not titrated, and after 8 days there is no sharp jump of the potential, although the colour of the $IrCl_6^{2-}$ appears after the first drops of $KMnO_4$ soln. are added. After boiling and cooling a soln. of $(NH_4)_3[IrCl_6]$ to room temp. neither a jump of potential nor the colour of $IrCl_6^{2-}$ is observed. On boiling aq. soln. of $(NH_4)_2[PtCl_4]$ under analogous conditions, no changes at all are observed, *i.e.*, the $PtCl_4^{2-}$ are completely titrated. This enables $PtCl_4^{2-}$ and $IrCl_6^{3-}$ to be determined when both are present in aq. soln. For this purpose, their total content is determined in one aliquot of the soln., and $PtCl_4^{2-}$ in another aliquot, the $IrCl_6^{3-}$ being calculated by difference. C. D. KOPKIN

2659. **Determination of the cement content of soil - cement. III. An investigation of some of the factors involved.** P. T. Sherwood (Road Res. Lab., Harmondsworth, Middx., England). *J. Appl. Chem.*, 1957, **7** (11), 596–604.—Sampling and the determination of Ca are discussed. The following three methods of determining CaO (after digestion of the sample in 6 *N* HCl) are compared—(*i*) removal of Fe and Al, pptn. of Ca as oxalate, followed by titration with $KMnO_4$; (*ii*) titration of an aliquot of the diluted digestion soln. with EDTA (disodium salt) in the presence of NaCN and Eriochrome blue - black as indicator; and (*iii*) flame photometry of a processed aliquot. For research work the EDTA method can replace the normal method with greater rapidity and no loss of accuracy, but for routine analyses of many samples the flame-photometric method is quicker than the EDTA and normal methods. The mean error in determining the content of cement by any of the three methods (after correcting for any CaO in the soil) is $\simeq -0{\cdot}2\%$. W. J. BAKER

See also Abstracts—**2483**, Extraction of elements. **2489**, Use of N-bromosuccinimide in oxidimetry. **2490**, Titrations with alkaline ferrocyanide. **2705**, Determination of metallic impurities in oils. **2726**, Determination of F in tissue. **2811**, Determination of Mn, Fe and Cu in plant material. **2833**, Apparatus for H_2O in sand, etc. **2863**, Determination of ^{137}Cs - ^{137}Ba in the presence of ^{95}Zr - ^{95}Nb.

3.—ORGANIC ANALYSIS

2660. **Rapid and precise carbon - hydrogen determination. Automatic macro combustion apparatus.** T. T. White, V. A. Campanile, E. J. Agazzi, L. D. TeSelle, P. C. Tait, F. R. Brooks and E. D. Peters (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 409–414.—The sample is alternately heated with a bare resistance-wire heater and cooled with an air blast to maintain the desired vaporisation rate while a stream of air flows over the sample. The heater and air blast are controlled by a mercury manometer which records pressure changes in the combustion tube. A roll of copper gauze is placed in the combustion tube and the tube introducing a secondary supply of O is extended into this roll. The copper is heated and thoroughly oxidised and the sample vapours are oxidised to a considerable extent by the copper oxide before they mix with the O; the copper oxide gauze also avoids depletion of O in the main furnace section of the tube and provides greater assurance of complete oxidation of the sample. Standard deviation values of $\pm 0{\cdot}03\%$ for C and $\pm 0{\cdot}02\%$ for H were obtained on a variety of materials, and recoveries were generally $\simeq 100\%$. Up to 24 analyses can be completed daily with a dual combustion unit. G. P. COOK

2661. **Analytical application of silver permanganate. VIII. Micro- and semi-micro determination of carbon and hydrogen in organic compounds containing fluorine.** J. Horáček and J. Körbl (Anal. Lab., Acad. Sci., Prague). *Chem. Listy*, 1957, **51** (11), 2132–2135.—When a layer of red lead is placed behind the layer of the decomposition product of silver permanganate in the combustion tube, C and H can be determined in organic compounds in the presence of F. The method was developed for 2 to 3 mg of the sample on a micro scale and 15 to 20 mg on a semi-micro scale. J. ZÝKA

2662. **Direct determination of oxygen in the elementary analysis of organic substances.** R. Fort (Lab. de Chim. Tinct., Conservatoire National des Arts et Métiers, Paris). *Chim. Anal.*, 1957, **39** (10), 366–374.—In this review article are discussed (*i*) difficulties and main sources of error, including nature of sample, exclusion of air, quality of the quartz combustion-tube, management of the furnace, quality of the contact carbon and of the "iodic anhydride," and blank corrections; (*ii*) methods of determination according to Schutz and Unterzaucher, together with some others, including an isotope-dilution method, in which ^{18}O is used; and (*iii*) methods employed in several Paris laboratories, which include the iodimetric method according to Unterzaucher and the gravimetric methods of Zimmermann and of Oita and Conway. (60 references.) R. E. ESSERY

2663. **Rapid quantitative determination of sulphur in organic compounds.** I. Lysyj and J. E. Zarembo (Food Machinery & Chem. Corp., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 428–430.—The method is based on the combustion of organic materials in an Erlenmeyer flask filled with oxygen which contains also a soln. of H_2O_2; SO_2 and SO_3 formed by the combustion react to form H_2SO_4. Excess of H_2O_2 and CO_2 is removed by boiling the reaction soln., and the H_2SO_4 is titrated with 0·02 *N* NaOH to methyl red indicator. Halogens, P, N and metals interfere with the titration, and in the presence of these elements the SO_4^{2-} are determined gravimetrically as $BaSO_4$. The accuracy and standard deviation for the titrimetric procedure are 100·15, $\pm 0{\cdot}57\%$, and for the gravimetric method 99·59, $\pm 0{\cdot}75\%$; each method was applied in triplicate to five compounds, some containing as much as 50% of S. G. P. COOK

2664. **Organic elementary analysis with micro-bomb. III. Gravimetric micro-determination of organic selenium.** Asaji Kondo (Lab. of Org. Chem., Tokyo Inst. of Tech., Okayama). *Japan Analyst*, 1957, **6** (9), 583–585.—Organic compounds (7 to 15 mg) containing Se are readily decomposed by heating with Na_2O_2 (0·5 g) in a micro-bomb (Elek, *J. Amer. Chem. Soc.*, 1953, **55**, 3439) for a few minutes. The product is dissolved in water (15 ml), neutralised with HCl, boiled with platinum wire (to catalyse the decomposition of H_2O_2), filtered, made 3 to 4 *N* in HCl and heated on a boiling-water bath with hydrazine soln. (0·1%, 2 ml) for 30 min. The ppt. is filtered off in a fine-glass filter (Alber, *J. Franklin Inst.*, 1939, **228**, 243), dried at 110° and weighed. K. SAITO

2665. **Modified needle valve for micro-Dumas determination of nitrogen.** S. P. Vango (Jet Propulsion Lab., Calif. Inst. of Technol., Pasadena, U.S.A.). *Chemist Analyst*, 1957, **46** (3), 72.—An improvement on the commercially available Hershberg - Southwell needle valve (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 404) prevents the expulsion of mercury through the threads between the valve stem and threaded gland by positive pressure or absorption of air by negative pressure. The mercury-sealed gland is put on the side away from the combustion tube, and a small stainless-steel valve replaces the knurled knob. An external mercury seal is added. R. L. MORTLOCK

2666. **Application of chelatometry to the determination of fluorine in organic compounds.** C. Hennart and E. Merlin (Orgasynthèse, Lab. de Vitry, Seine, France). *Anal. Chim. Acta*, 1957, **17** (5), 463–467 (in French).—Fluorine can be determined in a wide range of compounds, including *p*-fluorotoluene (17·2% of F) and poly(tetrafluoroethylene) (75·8% of F), by indirect titration with the disodium salt of EDTA. The sample is decomposed by heating with Na_2O_2 and a little ethanediol. The residue is dissolved in water, and the soln. is adjusted to a pH of 4 to 5 with acetic acid. The fluoride is pptd. by the addition of standard $CaCl_2$ soln. and filtered off. The excess of Ca is titrated in the presence of Eriochrome black T and a reagent comprising Mg - EDTA, NH_4Cl, NaCN and NH_3 in aq. soln. G. BURGER

2667. **Organic quantitative analysis. XVII. Determination of small amounts of chlorine and bromine in organic compounds.** M. Večeřa and A. Spěvák (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1957, **51** (11), 2037–2040.—The sample is ignited in a silica tube in a stream of O, the combustion products are absorbed in H_2O_2 and the chloride or bromide thus formed can be determined colorimetrically. *Procedure for calibration curve*—To the soln. containing 20 to 100 μg of NaCl in 25-ml flasks add $Hg(SCN)_2$ soln. (0·3% in methanol) (2 ml) and $NH_4Fe(SO_4)_2$ soln. (6% in 6 *N* HNO_3) (4 ml), make up to vol., and measure the extinction at 470 mμ. The method is rapid and suitable for solid and liquid organic compounds containing 0·01 to 2% of chlorine or bromine. J. ZÝKA

2668. **Sub-micro methods for the analysis of organic compounds. II. The determination of alkoxyl groups.** R. Belcher, M. K. Bhatty and T. S. West (Chem. Dept., The University, Birmingham, England). *J. Chem. Soc.*, 1957, (11), 4480–4482.—A micro-method for Zeisel determinations of alkoxyl groups in 45 to 60 μg of sample is described. The alkyl iodide is determined iodimetrically after oxidation to iodate with Br. *Procedure*—The gases from a small flask and reflux condenser pass through a scrubber containing 8 ml of Sb Na tartrate soln. and thence to an absorber containing 1 ml of Na acetate - acetic acid soln. and 4 drops of Br. The sample is weighed in a platinum cone and added to the reaction flask with 0·25 g of phenol and 0·5 ml of purified HI (*d* 1·7). Nitrogen is passed through the apparatus at the rate of 1 bubble per sec. in the scrubber and the flask is heated on a block for 60 to 90 min. at 220°. The contents of the absorber are transferred to a titration beaker and excess of Br is destroyed with formic acid. After addition of KI soln. the liberated iodine is titrated with 0·01 *N* $Na_2S_2O_3$, with Thyodene indicator. A syringe micro-burette and a magnetic stirrer are used. Individual results are within ± 0·03%. E. J. H. BIRCH

2669. **Determination of the thionyl group in organic compounds.** C. Hennart and E. Merlin (Orgasynthèse, Lab. de Vitry, Seine, France). *Chim. Anal.*, 1957, **39** (11), 429–431.—The sample is saponified with KOH to form an alkaline sulphite, from which the SO_2 is liberated with H_3PO_4 and distilled into excess of standard iodine soln., the excess being back-titrated with $Na_2S_2O_3$. An apparatus suitable for the determination is illustrated and manipulative details are given, including the method of handling substances that may react violently with KOH, resulting in the loss of SO_2, *e.g.*, acyl chlorides. Results for pentaerythritol cyclic mono- and di-sulphites, alone and in mixtures with pentaerythritol and its tetrachloride, and for $SOCl_2$ in mixtures with several acyl and alkyl chlorides, show satisfactory recoveries. R. E. ESSERY

2670. **Chromatographic analysis of C_1 to C_4 hydrocarbons and of certain non-hydrocarbon gases.** V. A. Sokolov and L. P. Kuz'mina (Inst. of Petroleum, USSR). *Zavod. Lab.*, 1957, **23** (9), 1034–1037.—The apparatus contains three columns, filled with different adsorbents and capable of being heated, into which the gas to be analysed—a mixture of H, CO, and saturated and unsaturated hydrocarbons C_1 to C_4—together with a carrier gas (CO_2 in the volume method and N in the thermal conductivity method) is passed successively. The gas is first freed from CO_2 (with 40% KOH soln.) and O (with alkaline pyrogallol soln.). The columns are each filled in three stages with reducing grain sizes (16, 8 and 4 mm) of the adsorbent. The first and third columns are 75 cm long and the second is 45 cm long. In one variant of the method the columns contain silica gel, activated carbon and kaolin (or natrolite, serpentine, etc.), respectively. With 3 to 6 ml of sample, C_2 and C_3 hydrocarbons are retained on the first column and are further separated when the column is heated (> 70°). The second column adsorbs H, CO and CH_4, and the third column adsorbs C_4 hydrocarbons. In another variant, the first column contains natrolite or serpentine to adsorb C_4 hydrocarbons from 6 to 8 ml of sample, the second column of silica gel then adsorbs C_2 and C_3 hydrocarbons, and the third column of activated carbon adsorbs H and CH_4. With synthetic mixtures the errors are ≃ 1 to 3% of the sample. G. S. SMITH

2671. **Resolution of isomeric hexanes by gas - liquid chromatography.** A. Zlatkis (Univ. of Houston, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 332–333.—Hexane isomers can be separated at

room temp. in < 30 min. on 250-cm columns of diatomaceous earth with various heterocyclic amines as the stationary phase. K. A. PROCTOR

2672. **Method of calibrating a scale of standards for the colorimetric determination of acetylene.** M. P. Korsh (All-Union Sci. Res. and Development Inst. for the Underground Gasification of Coal). *Zavod. Lab.*, 1957, **23** (11), 1299–1300.—The copper reagent soln. contains a stabiliser to give a stable soln. of copper acetylide for calibration purposes. Three reagents containing gelatin are recommended, and an apparatus designed for their use is described. G. S. SMITH

2673. **Chromatographic semi-micro analysis of gases. XIV. Direct determination of individual gaseous paraffins and olefins in buta-1:3-diene.** J. Janák and J. Novák (Lab. Anal. Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (10), 1832–1837.—A gas-chromatographic method is described by which individual paraffins and olefins in buta-1:3-diene are determined with an accuracy within 0·02% (abs.). The buta-1:3-diene is absorbed in a column containing maleic anhydride at 110°. The chromatographic separation is effected on a column of dimethylformamide with alusil (sodium aluminium silicate) at 20°. J. ZÝKA

2674. **Influence of olefin structure on bromine number as determined by various analytical methods.** E. H. Unger (Socony Mobil Oil Co. Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 375–380.—Three methods of determining olefins by bromination were tested. Two were tentative ASTM standard methods (D1158 and D1159) and the third was identical with the electrometric method (D1159) except that the $HgCl_2$ catalyst was omitted from the titration solvent. Forty-five API standard olefins were analysed and in general the modified D1159 method gave results which were closest to theoretical values; this method gave poorer results in the presence of appreciable amounts of sulphur, nitrogen and oxygen compounds. The deviations from the theoretical values for 41 mono-olefins averaged + 9·05, + 10·5 and − 0·64% for methods D1158, D1159 and modified D1159, respectively, and for the 4 diolefins ≃ − 35% for all three procedures. G. P. COOK

2675. **Chromatography of a mixture of hexane, chloroform and benzene on silica gel.** J. W. Blair and E. S. Amis (Univ. of Arkansas, Fayetteville, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 329–332.—An increase in the free water content of silica gel decreases its resolving power in the fractionation of a hexane - chloroform - benzene mixture. K. A. PROCTOR

2676. **Chromatographic analysis of organic peroxides.** M. H. Abraham, A. G. Davies, D. R. Llewellyn and E. M. Thain (Univ. Coll., London). *Anal. Chim. Acta*, 1957, **17** (5), 499–503 (in English).—Many organic peroxides can be identified by chromatography on paper that has been treated with a 5% soln. of silicone fluid M.S.1107 in *cyclo*hexane and baked at 110° for 1 hr. A mixture of $CHCl_3$, water and ethanol is used as the solvent. The spots are developed by spraying with acidified ferrous thiocyanate. Peroxides of low mol. wt., *e.g.*, *tert.*-butyl hydroperoxide, are too volatile for this method, and these can be identified and determined by gas - liquid partition chromatography on a column of 20-mesh kieselguhr coated with 30% of dinonyl phthalate. Nitrogen or air is used as the carrier gas. G. BURGER

2677. **Extractions with catechol and resorcinol.** R. Kubička and Z. Kvapil. *Chem. Tech., Berlin*, 1957, **9** (11), 661–666.—The addition compounds formed by resorcinol and catechol with alcohols, ketones and esters are stable to water and hydrocarbons, and may be used for separation of the O-containing compounds from hydrocarbons. Data are provided on the efficiency of extraction of several of the O-containing compounds from heptane soln., and on the influence of temp. and the presence of aromatics. More detailed results are given for the extraction of the ketonic components and acid oils from tar fractions. J. L. PROSSER

2678. **Estimation of acetaldehyde by hypoiodite oxidation.** Sameer Bose (Chem. Lab., Mahakoshal Mahabidyalaya, Jabalpur, M.P.). *J. Indian Chem. Soc.*, 1957, **34** (10), 739–742.—The determination is based on the oxidation of the acetaldehyde to acetic acid with a soln. of sodium hypoiodite containing an excess of free iodine. The reaction mixture is then acidified and the iodine liberated is titrated with thiosulphate. The error is ⩾ 0·8% and the method is applicable in the presence of acetone or ethanol. With slight modifications the method can be used for determining as little as 0·13 mg of the aldehyde. I. JONES

2679. **Determination of methyl vinyl ketone.** B. Buděšínský, K. Mňouček, F. Jančík and E. Kraus (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1957, **51** (10), 1819–1822.—*Bromimetric method*—Dissolve the sample (50 to 80 mg) in H_2O (15 ml), add a 0·1 *N* soln. of $KBrO_3$ - KBr (25 ml) and conc. HCl (10 ml), close the vessel and set it aside for 5 min. Determine the excess of the reagent iodimetrically and carry out a blank determination. *Hydroxylamine method*—Dissolve the sample (100 to 500 mg) in ethanol (96%) (15 ml), add bromophenol blue (2 to 3 drops) and neutralise with 0·1 *N* ethanolic KOH (blue colour). Add *N* hydroxylamine hydrochloride (5 ml) and set the soln. aside for 15 min. Titrate the liberated HCl with 0·1 *N* ethanolic KOH to a blue coloration. *Polarographic determination*—A well-developed polarographic wave, suitable for analytical purposes, is given in Britton - Robinson buffer soln., and this method has been found to be the most specific. The volatilisation of methyl vinyl ketone must be prevented. All three methods were found to be suitable for the determination of methyl vinyl ketone in admixture with its polymers. J. ZÝKA

2680. **Applications of chromatography in the field of organic acids.** J. Asselineau (Inst. de Biol. Phys.-chim., Paris). *Chim. Anal.*, 1957, **39** (10), 375–383.—A review article is presented in which are discussed (*i*), the isolation of the "acid fraction" from a complex mixture by adsorption chromatography or ion exchange, and (*ii*), the separation of the acids themselves, either (*a*), in groups according to unsaturation or other property, using adsorption or partition chromatography, ion exchange, or chromatography on urea for the separation of straight- and branched-chain acids, or (*b*), the separation of acids of a homologous series by adsorption, partition, column, paper or gas chromatography and ion exchange. Finally, the identification of the isolated acids may be made by comparison of their behaviour with that of known

compounds. When this method fails, clues to the structure of the unknown can be obtained by consideration of its behaviour in various chromatographic procedures. Reference is made to the quantity R_M, which is defined as log $(1/R_F - 1)$. This possesses additive properties, so that R_M values can be ascribed to various functional groups in the molecule, and used in structural studies. (116 references.) R. E. ESSERY

2681. **Improved iodimetric method of analysis for *tert.*-butyl per-esters.** L. S. Silbert and D. Swern (Eastern Reg. Res. Lab., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 385–387.—The Wheeler method for the iodimetric analysis of peroxides (*Oil & Soap*, 1932, **9**, 89) was modified for the analysis of both aliphatic and aromatic *tert.*-butyl per-esters. A soln. of 0·002% $FeCl_2.6H_2O$ in glacial acetic acid was used as solvent; this markedly accelerated the rate of liberation of iodine from the reaction of per-esters with iodide, with consequent improvement of the method. G. P. COOK

2682. **Determination of equivalent weight of esters and halides with cation-exchange resins.** W. H. Baldwin and C. E. Higgins (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 446–447.—Equivalent weights for several typical phosphorus or sulphur esters and alkyl halides were determined. The salts formed by heating these with ethanolamine were passed through cation-exchange resins (H form), and the free acid in the eluate was determined by titration with alkali. Results from the determination of 14 compounds were generally within ± 3% of theoretical. G. P. COOK

2683. **Detection of primary nitroparaffins in spot analysis.** F. Feigl and D. Goldstein (Min. da Agric., Rio de Janeiro, Brazil). *Z. anal. Chem.*, 1957, **158** (6), 427–429.—As little as 0·5 μg of nitromethane, nitroethane or nitropropane can be detected by mixing an ethanolic soln. (1 drop) with a freshly prepared saturated ethanolic soln. of Fast blue B (tetrazotised *o*-dianisidine) (1 drop) and 0·5 *N* aq. NaOH (1 drop); an orange spot or ring that rapidly turns red indicates the presence of a nitroparaffin. Organic compounds (such as phenols or aromatic amines) that react with diazonium salts in alkaline soln. interfere. A. R. ROGERS

2684. **Volumetric method for the determination of tetranitromethane in concentrated nitric acid.** Isamu Sakamaki, Hajime Ishikawa and Rikio Nakamura (Kurosaki Factory, Mitsubishi Chem. Ind., Yawata). *Japan Analyst*, 1957, **6** (10), 626–629.—Krauz's iodimetric titration of tetranitromethane (**I**) (*Chem. Obzor.*, 1937, **12**, 81) has been modified for application to the determination of **I** in HNO_3 (> 1 g per 50 ml). The time taken for quant. reaction between **I** and KI is markedly reduced by the addition of acetone. Nitrous acid is decomposed with sulphamic acid. The optimum pH value for the potentiometric titration (magic-eye titrator) of $Na_2S_2O_3$ with iodine soln. is 5·0 to 6·5. The error is ± 0·5 mg. *Procedure*—Weigh the sample (5 to 10 ml) in a thin glass bulb and crush this in acetone (100 ml) containing 10% sulphamic acid (3 ml). Add $NaHCO_3$ (the same weight as the sample) and water until the salts dissolve. Adjust the pH to between 5·0 and 6·5 with $NaHCO_3$ (glass electrode), add KI (2 g), McIlvain's buffer (pH 4·8) (10 ml) and a known amount of 0·1 *N* $Na_2S_2O_3$, and back-titrate the excess with iodine soln. (platinum electrode). K. SAITO

2685. **Potentiometric determination of primary aromatic amines.** R. S. Saxena and C. S. Bhatnagar [Chemical Lab., Gov. College, Kota (Rajasthan)]. *Naturwissenschaften*, 1957, **44** (22), 583–584 (in English).—In dilute soln. and at temperatures below 30°, primary aromatic amines (*e.g.*, aniline) can be titrated in the presence of HCl with a $NaNO_2$ soln. and the end-point in the titration registered potentiometrically, the Cambridge pH meter being used. An indicator electrode of bright platinum foil was satisfactory. E. KAWERAU

2686. **Diethylenetetra-ammonium sulphatocerate as volumetric reagent. V. Determination of organic derivatives of hydrazine by the iodine chloride method.** Balwant Singh (Panjap Univ. Coll., Hoshiapur, India). *Anal. Chim. Acta*, 1957, **17** (5), 467–469 (in English).—To the hydrazine derivative are added H_2O (25 ml), HCl (60 ml), 0·02 *M* ICl (5 ml) and $CHCl_3$ (5 ml). The soln. is titrated with 0·02 *N* diethylenetetra-ammonium sulphatocerate in 2 *N* H_2SO_4. The flask is shaken vigorously between additions of titrant. The end-point is indicated by a change from violet to very pale yellow in the $CHCl_3$ layer. G. BURGER

2687. **Coulometric determination of thiols separated by gas chromatography.** A. Liberti and G. P. Cartoni (Inst. of Anal. Chem., Univ. of Messina, Italy). *Chim. e Ind.*, 1957, **39** (10), 821–824.—Aliphatic thiols (*e.g.*, in petroleum distillates) may be separated by extraction with KOH - ethanol, hydrolysis, extraction with *iso*pentane, and vapour-phase chromatography on a Celite - Silicone DC550 - stearic acid column. The issuing gases are bubbled into a cell containing 75% ethanol and 10^{-4} *M* Ag^+ and fitted with a S.C.E., silver anode, platinum cathode and rotating platinum electrode. Reaction with the individual thiols results in a decrease of Ag^+ content as measured coulometrically by the rotating platinum electrode, and the thiol content can thus be calculated. A. G. COOPER

2688. **Infra-red identification of some sulphur derivatives of long-chain fatty acids.** H. Susi, N. H. Koenig, W. E. Parker and D. Swern (U.S. Dept. Agric., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 443–446.—The spectral effects produced by introducing sulphide, sulphoxide or sulphone groups into the fatty-acid chain are described. Interruption of the carbon chain by these groups makes the band progression region less useful for chain-length determination, but introduces spectral detail which can be used to identify individual compounds. Very closely related sulphur derivatives of fatty acids can be distinguished by studying the 1350 to 1180 cm^{-1} region of solid-state spectra obtained with potassium bromide pellets. Differentiation of the main classes can be achieved by utilising the dilute-soln. spectra of the corresponding methyl esters. Spectra of all the groups are illustrated. G. P. COOK

2689. **Field sampling and analysis of micro quantities of sesquimustard [di-(2-chloroethylthio)ethane] in presence of mustard [gas].** A. Koblin (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 430–432.—Both compounds are analysed by two different techniques and, from the simultaneous equations derived from the slopes of

room temp. in < 30 min. on 250-cm columns of diatomaceous earth with various heterocyclic amines as the stationary phase. K. A. PROCTOR

2672. **Method of calibrating a scale of standards for the colorimetric determination of acetylene.** M. P. Korsh (All-Union Sci. Res. and Development Inst. for the Underground Gasification of Coal). *Zavod. Lab.*, 1957, **23** (11), 1299–1300.—The copper reagent soln. contains a stabiliser to give a stable soln. of copper acetylide for calibration purposes. Three reagents containing gelatin are recommended, and an apparatus designed for their use is described. G. S. SMITH

2673. **Chromatographic semi-micro analysis of gases. XIV. Direct determination of individual gaseous paraffins and olefins in buta-1:3-diene.** J. Janák and J. Novák (Lab. Anal. Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (10), 1832–1837.—A gas-chromatographic method is described by which individual paraffins and olefins in buta-1:3-diene are determined with an accuracy within 0·02% (abs.). The buta-1:3-diene is absorbed in a column containing maleic anhydride at 110°. The chromatographic separation is effected on a column of dimethylformamide with alusil (sodium aluminium silicate) at 20°. J. ZÝKA

2674. **Influence of olefin structure on bromine number as determined by various analytical methods.** E. H. Unger (Socony Mobil Oil Co. Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 375–380.—Three methods of determining olefins by bromination were tested. Two were tentative ASTM standard methods (D1158 and D1159) and the third was identical with the electrometric method (D1159) except that the $HgCl_2$ catalyst was omitted from the titration solvent. Forty-five API standard olefins were analysed and in general the modified D1159 method gave results which were closest to theoretical values; this method gave poorer results in the presence of appreciable amounts of sulphur, nitrogen and oxygen compounds. The deviations from the theoretical values for 41 mono-olefins averaged + 9·05, + 10·5 and − 0·64% for methods D1158, D1159 and modified D1159, respectively, and for the 4 diolefins ≃ − 35% for all three procedures. G. P. COOK

2675. **Chromatography of a mixture of hexane, chloroform and benzene on silica gel.** J. W. Blair and E. S. Amis (Univ. of Arkansas, Fayetteville, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 329–332.—An increase in the free water content of silica gel decreases its resolving power in the fractionation of a hexane - chloroform - benzene mixture. K. A. PROCTOR

2676. **Chromatographic analysis of organic peroxides.** M. H. Abraham, A. G. Davies, D. R. Llewellyn and E. M. Thain (Univ. Coll., London). *Anal. Chim. Acta*, 1957, **17** (5), 499–503 (in English).—Many organic peroxides can be identified by chromatography on paper that has been treated with a 5% soln. of silicone fluid M.S.1107 in *cyclo*hexane and baked at 110° for 1 hr. A mixture of $CHCl_3$, water and ethanol is used as the solvent. The spots are developed by spraying with acidified ferrous thiocyanate. Peroxides of low mol. wt., *e.g.*, *tert.*-butyl hydroperoxide, are too volatile for this method, and these can be identified and determined by gas - liquid partition chromatography on a column of 20-mesh kieselguhr coated with 30% of dinonyl phthalate. Nitrogen or air is used as the carrier gas. G. BURGER

2677. **Extractions with catechol and resorcinol.** R. Kubička and Z. Kvapil. *Chem. Tech., Berlin*, 1957, **9** (11), 661–666.—The addition compounds formed by resorcinol and catechol with alcohols, ketones and esters are stable to water and hydrocarbons, and may be used for separation of the O-containing compounds from hydrocarbons. Data are provided on the efficiency of extraction of several of the O-containing compounds from heptane soln., and on the influence of temp. and the presence of aromatics. More detailed results are given for the extraction of the ketonic components and acid oils from tar fractions. J. L. PROSSER

2678. **Estimation of acetaldehyde by hypoiodite oxidation.** Sameer Bose (Chem. Lab., Mahakoshal Mahabidyalaya, Jabalpur, M.P.). *J. Indian Chem. Soc.*, 1957, **34** (10), 739–742.—The determination is based on the oxidation of the acetaldehyde to acetic acid with a soln. of sodium hypoiodite containing an excess of free iodine. The reaction mixture is then acidified and the iodine liberated is titrated with thiosulphate. The error is ⩾ 0·8% and the method is applicable in the presence of acetone or ethanol. With slight modifications the method can be used for determining as little as 0·13 mg of the aldehyde. I. JONES

2679. **Determination of methyl vinyl ketone.** B. Buděšínský, K. Mňouček, F. Jančik and E. Kraus (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1957, **51** (10), 1819–1822.—*Bromimetric method*—Dissolve the sample (50 to 80 mg) in H_2O (15 ml), add a 0·1 *N* soln. of $KBrO_3$ - KBr (25 ml) and conc. HCl (10 ml), close the vessel and set it aside for 5 min. Determine the excess of the reagent iodimetrically and carry out a blank determination. *Hydroxylamine method*—Dissolve the sample (100 to 500 mg) in ethanol (96%) (15 ml), add bromophenol blue (2 to 3 drops) and neutralise with 0·1 *N* ethanolic KOH (blue colour). Add *N* hydroxylamine hydrochloride (5 ml) and set the soln. aside for 15 min. Titrate the liberated HCl with 0·1 *N* ethanolic KOH to a blue coloration. *Polarographic determination*—A well-developed polarographic wave, suitable for analytical purposes, is given in Britton - Robinson buffer soln., and this method has been found to be the most specific. The volatilisation of methyl vinyl ketone must be prevented. All three methods were found to be suitable for the determination of methyl vinyl ketone in admixture with its polymers. J. ZÝKA

2680. **Applications of chromatography in the field of organic acids.** J. Asselineau (Inst. de Biol. Phys.-chim., Paris). *Chim. Anal.*, 1957, **39** (10), 375–383.—A review article is presented in which are discussed (*i*), the isolation of the "acid fraction" from a complex mixture by adsorption chromatography or ion exchange, and (*ii*), the separation of the acids themselves, either (*a*), in groups according to unsaturation or other property, using adsorption or partition chromatography, ion exchange, or chromatography on urea for the separation of straight- and branched-chain acids, or (*b*), the separation of acids of a homologous series by adsorption, partition, column, paper or gas chromatography and ion exchange. Finally, the identification of the isolated acids may be made by comparison of their behaviour with that of known

compounds. When this method fails, clues to the structure of the unknown can be obtained by consideration of its behaviour in various chromatographic procedures. Reference is made to the quantity R_M, which is defined as log $(1/R_F - 1)$. This possesses additive properties, so that R_M values can be ascribed to various functional groups in the molecule, and used in structural studies. (116 references.) R. E. ESSERY

2681. **Improved iodimetric method of analysis for *tert.*-butyl per-esters.** L. S. Silbert and D. Swern (Eastern Reg. Res. Lab., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 385–387.—The Wheeler method for the iodimetric analysis of peroxides (*Oil & Soap*, 1932, **9**, 89) was modified for the analysis of both aliphatic and aromatic *tert.*-butyl per-esters. A soln. of 0·002% $FeCl_2.6H_2O$ in glacial acetic acid was used as solvent; this markedly accelerated the rate of liberation of iodine from the reaction of per-esters with iodide, with consequent improvement of the method. G. P. COOK

2682. **Determination of equivalent weight of esters and halides with cation-exchange resins.** W. H. Baldwin and C. E. Higgins (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 446–447.—Equivalent weights for several typical phosphorus or sulphur esters and alkyl halides were determined. The salts formed by heating these with ethanolamine were passed through cation-exchange resins (H form), and the free acid in the eluate was determined by titration with alkali. Results from the determination of 14 compounds were generally within ± 3% of theoretical. G. P. COOK

2683. **Detection of primary nitroparaffins in spot analysis.** F. Feigl and D. Goldstein (Min. da Agric., Rio de Janeiro, Brazil). *Z. anal. Chem.*, 1957, **158** (6), 427–429.—As little as 0·5 μg of nitromethane, nitroethane or nitropropane can be detected by mixing an ethanolic soln. (1 drop) with a freshly prepared saturated ethanolic soln. of Fast blue B (tetrazotised *o*-dianisidine) (1 drop) and 0·5 *N* aq. NaOH (1 drop); an orange spot or ring that rapidly turns red indicates the presence of a nitroparaffin. Organic compounds (such as phenols or aromatic amines) that react with diazonium salts in alkaline soln. interfere. A. R. ROGERS

2684. **Volumetric method for the determination of tetranitromethane in concentrated nitric acid.** Isamu Sakamaki, Hajime Ishikawa and Rikio Nakamura (Kurosaki Factory, Mitsubishi Chem. Ind., Yawata). *Japan Analyst*, 1957, **6** (10), 626–629.—Krauz's iodimetric titration of tetranitromethane (**I**) (*Chem. Obzor.*, 1937, **12**, 81) has been modified for application to the determination of **I** in HNO_3 (> 1 g per 50 ml). The time taken for quant. reaction between **I** and KI is markedly reduced by the addition of acetone. Nitrous acid is decomposed with sulphamic acid. The optimum pH value for the potentiometric titration (magic-eye titrator) of $Na_2S_2O_3$ with iodine soln. is 5·0 to 6·5. The error is ± 0·5 mg. *Procedure*—Weigh the sample (5 to 10 ml) in a thin glass bulb and crush this in acetone (100 ml) containing 10% sulphamic acid (3 ml). Add $NaHCO_3$ (the same weight as the sample) and water until the salts dissolve. Adjust the pH to between 5·0 and 6·5 with $NaHCO_3$ (glass electrode), add KI (2 g), McIlvain's buffer (pH 4·8) (10 ml) and a known amount of 0·1 *N* $Na_2S_2O_3$, and back-titrate the excess with iodine soln. (platinum electrode). K. SAITO

2685. **Potentiometric determination of primary aromatic amines.** R. S. Saxena and C. S. Bhatnagar [Chemical Lab., Gov. College, Kota (Rajasthan)]. *Naturwissenschaften*, 1957, **44** (22), 583–584 (in English).—In dilute soln. and at temperatures below 30°, primary aromatic amines (*e.g.*, aniline) can be titrated in the presence of HCl with a $NaNO_2$ soln. and the end-point in the titration registered potentiometrically, the Cambridge pH meter being used. An indicator electrode of bright platinum foil was satisfactory. E. KAWERAU

2686. **Diethylenetetra-ammonium sulphatocerate as volumetric reagent. V. Determination of organic derivatives of hydrazine by the iodine chloride method.** Balwant Singh (Panjap Univ. Coll., Hoshiapur, India). *Anal. Chim. Acta*, 1957, **17** (5), 467–469 (in English).—To the hydrazine derivative are added H_2O (25 ml), HCl (60 ml), 0·02 *M* ICl (5 ml) and $CHCl_3$ (5 ml). The soln. is titrated with 0·02 *N* diethylenetetra-ammonium sulphatocerate in 2 *N* H_2SO_4. The flask is shaken vigorously between additions of titrant. The end-point is indicated by a change from violet to very pale yellow in the $CHCl_3$ layer. G. BURGER

2687. **Coulometric determination of thiols separated by gas chromatography.** A. Liberti and G. P. Cartoni (Inst. of Anal. Chem., Univ. of Messina, Italy). *Chim. e Ind.*, 1957, **39** (10), 821–824.—Aliphatic thiols (*e.g.*, in petroleum distillates) may be separated by extraction with KOH - ethanol, hydrolysis, extraction with *iso*pentane, and vapour-phase chromatography on a Celite - Silicone DC550 - stearic acid column. The issuing gases are bubbled into a cell containing 75% ethanol and 10^{-4} *M* Ag^+ and fitted with a S.C.E., silver anode, platinum cathode and rotating platinum electrode. Reaction with the individual thiols results in a decrease of Ag^+ content as measured coulometrically by the rotating platinum electrode, and the thiol content can thus be calculated. A. G. COOPER

2688. **Infra-red identification of some sulphur derivatives of long-chain fatty acids.** H. Susi, N. H. Koenig, W. E. Parker and D. Swern (U.S. Dept. Agric., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 443–446.—The spectral effects produced by introducing sulphide, sulphoxide or sulphone groups into the fatty-acid chain are described. Interruption of the carbon chain by these groups makes the band progression region less useful for chain-length determination, but introduces spectral detail which can be used to identify individual compounds. Very closely related sulphur derivatives of fatty acids can be distinguished by studying the 1350 to 1180 cm^{-1} region of solid-state spectra obtained with potassium bromide pellets. Differentiation of the main classes can be achieved by utilising the dilute-soln. spectra of the corresponding methyl esters. Spectra of all the groups are illustrated. G. P. COOK

2689. **Field sampling and analysis of micro quantities of sesquimustard [di-(2-chloroethylthio)ethane] in presence of mustard [gas].** A. Koblin (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 430–432.—Both compounds are analysed by two different techniques and, from the simultaneous equations derived from the slopes of

the colorimeter calibration curves, the concn. of each can be determined. *o*-Dianisidine and Cu acetate were the reagents used in one of the procedures and 4-(4-nitrobenzyl)pyridine was used in the other. Recoveries > 90% with an accuracy of ± 3% in the 75-μg range were obtained with several mixtures of mustard gas and sesquimustard.
G. P. Cook

2690. **Multiple colour reactions for aromatic hydrocarbons.** W. Albersmeyer and G. Krampitz (Inst. f. Anatomie u. Physiologie der Haustiere der Univ., Bonn, Germany). *Naturwissenschaften*, 1957, **44** (17), 466–467.—Since the R_F values of many aromatic hydrocarbons are not constant, the location by colour reagents is of importance for their identification on chromatograms. Seven substances known to yield colours with aromatic hydrocarbons [*e.g.*, $CuSO_4$, $CuSO_4$ plus picric acid, Ehrlich's reagent, $K_4Fe(CN)_6$] are listed together with their colour reactions with 1-methylnaphthalene, quinoline, *iso*quinoline, 2-methylquinoline, 2:4-lutidine, 2:5-lutidine, α-picoline, γ-picoline and 4-methylquinoline.
E. Kawerau

2691. **The non-aqueous titration of phenolic compounds.** J. Allen and E. T. Geddes (The British Drug Houses Ltd., Graham Street, London). *J. Pharm. Pharmacol.*, 1957, **9** (12), 990–996.—Dissolve the sample in neutralised dimethylformamide and dilute an aliquot containing about 0·5 milli-equiv. to about 25 ml. Titrate potentiometrically (glass electrode and sleeve-type S.C.E.) with 0·1 *N* tetrabutylammonium hydroxide in benzene - methanol, with magnetic stirring. The height of the step in the curve relating e.m.f. and vol. of titrant is about 100 to 150 mV for most of the phenolic substances titrated. The lower limit of practicability is represented by resorcinol, with a step of about 75 mV. Polyhydric phenols give only one inflection point sufficiently well marked to be used as an indication of the end-point.
A. R. Rogers

2692. **Chromatography of aromatic isomers. VII. Separation of some mono- and di-carboxylic acids.** J. Franc (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1957, **51** (11), 2041–2047.—A method of separating the nitro derivatives of some benzene mono- and di-carboxylic acids is described. Paper chromatography was used for the quant. determination of *iso*phthalic acid in the presence of terephthalic acid. The relation between dipole moment and chromatographic behaviour was used for the identification of some separated nitrocarboxylic acids. The ΔK values for $-CH_3$, $-COOH$, $-COOCH_3$ and $-NO_2$ groups were determined in all the solvents used.
J. Zýka

2693. ***p*-Dimethylaminobenzaldehyde as a reagent for the characterisation of primary aromatic amines.** J. Kolšek, N. Novak and M. Perpar (Inst. for Org. Chem., Univ., Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1957, **159** (2), 113–117.—*p*-Dimethylaminobenzaldehyde is a suitable reagent for the characterisation of primary, though not of secondary and tertiary, aromatic amines. The resulting Schiff's bases are formed rapidly, are sparingly sol. in H_2O, and their m.p. are high and sharp. The derivatives are suitably prepared from dil. acid soln., since their hydrochlorides are also sparingly soluble. The m.p. of the salts are considerably higher than those of the free bases, so for identification the free bases are liberated with aq. NH_3. A table is given of m.p. of the Schiff's bases formed by several aromatic primary amines.
J. H. Waton

2694. **Iminotetrazolium salts. Identification of sulphonic acids.** R. M. Herbst and K. G. Stone (Kedzie Chem. Lab., State Univ., East Lansing, Mich.). *J. Org. Chem.*, 1957, **22** (10), 1139–1142.—1-*n*-Octyl-4-benzyl-5-iminotetrazolinium ditartrate monohydrate (OBIT) is suggested as a reagent for the identification of sulphonic acids or their sodium salts. The insolubility of most of the sulphonates in water suggests that they might be adaptable to quant. determinations.
N. E.

2695. **Gas - liquid partition chromatography of mixtures of the three isomeric methylcyclohexenes and methylenecyclohexane.** E. Gil-Av, J. Herling and J. Shabtai (Daniel Sieff Res. Inst., Weizmann Inst. of Sci., Rehovoth, Israel). *Chem. & Ind.*, 1957, (45), 1483–1484.—Experimental details are given for the separation of these mixtures. Helium is used as the carrier gas and a soln. of glycol saturated with $AgNO_3$ supported on Sterchamol as the stationary phase. It is claimed that each component can be estimated to an accuracy of within ± 1% of the total.
G. S. Roberts

2696. **Benzal [benzylidene] chloride test for hetero substituted aromatic compounds.** E. Sawicki (Robert A. Taft Sanitary Engng Centre, Cincinnati, Ohio, U.S.A.). *Chemist Analyst*, 1957, **46** (3), 67–69.—Dissolve a few crystals or drops of the aromatic compound in a small vol. of $CHCl_3$, and add about 5 ml of trifluoroacetic acid (**I**) and one drop of benzylidene chloride. Shake till homogeneous, set aside for 3 min., add one drop of H_2SO_4, shake, and note the colour. With a negative result, slant the tube and run 2 further drops of H_2SO_4 into the mixture. If a colour forms near the H_2SO_4 layer it indicates that a positive result can be obtained. Shake for 5 to 10 min. and note the colour. To determine the extinction, a Beckman DU spectrophotometer is used with the test soln. suitably diluted with **I**. Most compounds are $CHCl_3$-sol. as is **I**, which is a relatively strong acid of $pK = 0·3$. Many N-acyl polynuclear aromatic amines were tested because their acyl derivatives and/or parent amine show animal carcinogenic activity, and a colour test would be of value. A list of compounds tested and absorption maxima is given.
R. L. Mortlock

2697. **Colorimetric determination of naphthalene-2:6- and -2:7-disulphonic acids in nickel electrolytes.** V. P. Persiantseva and V. A. Shnelder (D. I. Mendeleev Chem.-Tech. Inst.). *Zavod. Lab.*, 1957, **23** (11), 1298.—The Ni is removed from the electrolyte (5 ml diluted to 20 to 25 ml) by passage through a column of SDV-3 and the filtrate, in a platinum dish, is treated with 10 ml of 30% NaOH soln. and evaporated to dryness. The residue is fused at 320° ± 2° for 10 to 15 min., the cooled melt is treated with 35 ml of a nitrating mixture (10 g of NH_4NO_3 in 100 ml of conc. H_2SO_4), the liquid after cessation of the violent reaction is diluted to 100 ml with water and the extinction is determined with a blue colour filter. The results are calculated from a calibration curve.
G. S. Smith

2698. **Rapid determination of anthracene by the diene method.** Tsugio Takeuchi and Motohisa Furusawa (Dept. of Applied Chem., Fac. of Engng, Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1957, **6** (10) 621–625.—In order to

minimise the time taken for the determination of anthracene (**I**) in the presence of carbazole or phenanthrene, the excess of maleic anhydride (**II**) is extracted with water, the xylene (solvent) being retained below the aq. layer by the addition of CCl_4. The addition compound of **I** and **II** does not interfere with the alkalimetric titration of the excess of **II**. The time taken for an estimation is $\simeq$ 1 hr. *Procedure*—Boil the sample (0·5 g) and **II** ($\simeq$ 0·5 g, less than the amount of **I**) in xylene (10 ml) for 10 min., cool, and add CCl_4 (5 ml) and water (90 ml). Titrate the aq. layer with 0·25 *N* NaOH with a mixture of cresol red and thymol blue (1:3 by vol. of 0·1% aq. soln. neutralised with NaOH) as indicator. The purity of **II** must be determined by alkalimetric titration in 100 ml of water.

K. SAITO

2699. **Polarographic estimation of tetracene.** A. M. Wild (Armament Res. and Devel. Estab., Min. of Supply, Swynnerton, Staffs., England). *Chem. & Ind.*, 1957, (47), 1543.—Tetracene (1-5′-tetrazolyl-4-amidinotetrazene), gives a well-defined reduction-wave at the dropping mercury electrode, whose height is proportional to concn. over the range $1{\cdot}0 \times 10^{-3}$ *M* to $1{\cdot}4 \times 10^{-4}$ *M* ($E_{\frac{1}{2}}$ *vs.* the mercury pool = − 0·34 to − 0·37 V). The sample (> 10 mg) is dissolved in 10 ml of 2·6 *M* HCl and transferred to a flask containing 10 ml of 0·867 *M* Na tartrate and 0·5 ml of 0·5% aq. gelatin soln., mixed thoroughly and polarographed at 25° from − 0·2 to − 0·6 V. Results are compared with polarograms from a standard soln. of tetracene. Soln. should be measured within 3 hr. of being made up. Products of hydrolysis of tetracene do not interfere.

R. E. ESSERY

2700. **Extension of the fluorescent indicator adsorption method to the estimation of the four main hydrocarbon groups in light petroleum fractions.** K. Schindel (Österreich. Mineralölverwaltung A.-G., Wien I, Reichsratstr. 1, Austria). *Erdöl u. Kohle*, 1957, **10** (11), 754–757.—In the usual fluorescent indicator adsorption method, light petroleum fractions are separated into three groups, *viz*, aromatics, olefins and naphthenes plus paraffins, on a silica-gel column. The volumetric ratio of these groups is measured by the length of the respective zones, rendered visible by a fluorescent indicator. Extending this method, the zone containing naphthenes and paraffins can be collected separately, and the ratio of the two types estimated from the refractive index with the aid of nomograms (Zerbe, "*Mineralöle u. verwandte Producte*," Berlin, 1952) to within ± 5%. The PONA method, with which the present method is compared, is equally precise for straight-run distillates, but less so for cracked fractions since the refractive index is not measured but estimated from assumptions that may be considerably in error when olefins are present.

G. BURGER

2701. **Mass spectrometer-type analysis for olefins in gasoline.** L. Mikkelsen, R. L. Hopkins and D. Y. Yee (Petroleum Expt. Sta., U.S. Dept. of the Interior, Bartlesville, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 317–321.—Benzenesulphinyl chloride reacts quant. with olefins in a hydrocarbon mixture to form a high-boiling addition product which does not contribute to the mass spectrum of the non-olefinic components. By comparing mass spectra before and after treatment with this reagent, the olefin, monocycloparaffin, "coda" (cyclomono-olefins, diolefins and acetylenes) and dicycloparaffin mass peaks may be determined separately. The accuracy is comparable to that of fluorescent indicator adsorption and bromine value analyses for samples of low olefin content and probably better in some other cases.

K. A. PROCTOR

2702. **Direct determination of isoparaffins and normal paraffins in olefin-free gasoline by mass spectrometer.** W. C. Ferguson and H. E. Howard (Union Oil Co. of California, Brea, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 314–317.—The value of this method, which can be applied to any 100° to 400° F hydrocarbon mixture containing < 3% of olefin, lies in its ability to show direct changes in the isoparaffin to normal paraffin ratio as a result of various processes. Data from a single mass-spectrometer run are used, and the procedure adds < 30 min. to a hydrocarbon-type analysis. The accuracy is estimated to be within ± 10% in most cases.

K. A. PROCTOR

2703. **Separation of 132° to 138° C fraction of petroleum. Bicycloparaffins in gasoline fraction of petroleum.** B. J. Mair, P. E. Eberly, jun., N. C. Krouskop and F. D. Rossini (Carnegie Inst. Technol., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 393–399.—The branched paraffin - cycloparaffin portion of the representative petroleum of the API research project 6, normally boiling in the range 132° to 138°, was separated by regular and azeotropic distillation to give concentrates of branched paraffins, monocycloparaffins and bicycloparaffins. From the bicycloparaffin fraction two compounds were isolated and identified—*cis*-bi*cyclo*[3:3:0]-octane at 137·1°, and bi*cyclo*[3:2:1]octane near 138°. Their concn. in crude petroleum were estimated at 0·06 and 0·008% by vol., respectively. In addition, two other bicycloparaffins isolated from previous work were tentatively identified, the one boiling near 124·5° as one of the four isomers of methylbi*cyclo*[2:2:1]heptane and the other at 146·7° as one of the four isomers of ethylbi*cyclo*[2:2:1]heptane or one of the nine isomers of methylbi*cyclo*[3:3:0]octane.

G. P. COOK

2704. **Wet-ash spectrochemical method for determination of trace metals in petroleum fractions.** J. Hansen and C. R. Hodgkins (Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 368–372.—In the procedure described, the sample (admixed with 40 mg of copper powder as carrier-matrix) is decomposed by digestion with glycerol and conc. H_2SO_4 at $\simeq$ 400°, the residue is ignited at $\simeq$ 540°, mixed with 40 mg of graphite powder, and the V, Ni and Fe (0·5 to 50 μg of each) are determined by emission spectrometry in either the photographic or direct-reading instrument. A conversion chart of recorder-deflections *vs.* μg is advised; coeff. of variation for V and Ni are between 8 and 12%, but are much wider for Fe. The lower limit of determination is 0·05 p.p.m. of Ni or V. A batch of 20 to 25 samples can be analysed in 0·75 to 1·5 man-hours per sample.

W. J. BAKER

2705. **Spectrographic determination of metallic impurities in oils.** E. V. Il'ina. *Trudy Leningr. Voen-Mekhan. Inst.*, 1956, (5), 68–72; *Ref. Zhur., Khim.*, 1957, Abstr. No. 69,189.—To study the wear of engine parts, a method is evolved for determining Fe, Al, Cu, Sn, Pb and Si in oil. Weigh 3 g of the oil into a crucible, add 2 ml of Ni oleate and 1 ml of Ba oleate dissolved in petrol and 100 mg of powdered graphite. Ignite the contents of the crucible, dry the residue at 800°, add 200 mg of powdered graphite and grind in a mortar. Excite the spectra in an a.c. arc discharge at 10 amp. by

evaporation of the substance in a groove in the carbon electrode. The analytical lines used are Fe 2953·9 and Ni 2892·6, Al 3092·7 and Ni 3134·1, Cu 3274·0 and Ni 3134·1, Si 2881·6 and Ni 2892·6, Sn 3262·3 and Ni 3134·1, and Pb 2833·1 and Ni 2892·6 A. The minimum concn. which may be determined is 0·01%. Prepare the standards synthetically. The error of the analysis is ± 20%.
C. D. KOPKIN

2706. **Determination of 3:4-benzopyrene in exhaust gases of diesel engines.** K. Johne, I. Kleiss and A. Reuter (Battelle Inst., Frankfurt-am-Main). *Angew. Chem.*, 1957, **69** (21), 675.—The material extracted with benzene from a sampling filter is dissolved in *cyclo*hexane and a chromatogram is developed on alumina with a mixture of light petroleum and ether (10:1). The zone containing 3:4-benzopyrene may also contain 1:12-benzoperylene, which has similar u.v. absorption and fluorescence. This fraction is collected by washing the column with ether, and the 3:4-benzopyrene is separated by ascending chromatography on acetylated paper with a solvent mixture of methanol - ether - water (4:4:1). Sharp separation is obtained in the range 0·1 to 20 μg of 3:4-benzopyrene. As little as 0·1 μg can be detected by fluorescence under u.v., and determined by comparison with standards. For quant. determination, the zone is cut out and extracted with boiling ether and then with methanol - pyridine (10:1). After evaporation of the solvent, the extract is dissolved in *cyclo*hexane and the extinction measured at 364 and 384 mμ. The spectrum is examined from 270 to 310 mμ as a check on purity. G. BURGER

2707. **Automatic unit for determination of volatile matter in coal, coke and char.** R. P. Hensel and S. A. Jones (Pittsburgh Consolidation Coal Co., Library, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 402–404.—The ASTM designates a 7-min. heating time at 950° for the determination of volatile matter. Conventional manual control prevents close duplication of heating rates and results are often erratic. To avoid this, an automatic volatile matter unit is described which consists essentially of a mechanical lowering device for the crucible with automatic timing of heating. Replicate analysis on three materials gave a maximum probable error of ≃ 0·11%, which was superior to the results obtained by manual operation.
G. P. COOK

2708. **Formulae for estimation of alcoholic constituents in synthetic mixtures and essential oils. V. System consisting of two primary alcohols, an ester, a ketone and a hydrocarbon.** K. Narain and J. B. Lal (H.B. Technol. Inst., Kanpur, India). *J. Oil Technol. Ass., India*, 1956, **12** (2), 135–142.—Theoretical equations have been derived from the use of double acylation, *e.g.*, acetylation and butyrylation, for the determination of two primary or secondary alcohols in a mixture containing two alcohols, an ester, a ketone and a hydrocarbon. It is shown that the ester value after butyrylation can be expressed in terms of the ester value before and after acetylation; this indicates that butyrylation and acetylation do not constitute two independent operations for the determination of two individual alcohols present in a mixture.
G. R. WHALLEY

2709. **Physico-chemical methods for estimation of esters and alcohols in essential oils and synthetic blends. III.** S. P. Srivastava, D. Prakash and J. B. Lal (H. B. Technol. Inst., Kanpur, India). *J. Oil Technol. Ass., India*, 1956, **12** (2), 95–102.—Four independent equations are theoretically derived to evaluate four variables in a quaternary mixture of three alcohols and one ester, or three esters and one alcohol. The first two equations are based on the ester value before and after acetylation, the third on the percentage composition of the mixture, whilst the final equation involves the additive nature of the specific vol. of the components. Hence it is possible to determine the percentage composition by determining ester values and specific gravity. G. R. WHALLEY

2710. **Interfering action of esters other than acetates in the estimation of alcohols in synthetic mixtures by acetylation. I.** G. M. Mathur, J. B. Lal, V. N. Nigam and S. N. Kapoor (H.B. Technol. Inst., Kanpur, India). *J. Oil Technol. Ass., India*, 1956, **12** (2), 115–118.—The determination of benzyl alcohol in the presence of benzyl benzoate has been carried out by acetylation. About 10 ml of the sample is heated with 15 ml of acetic anhydride and 1 g of Na acetate at 140° to 145° for 2 hr., 50 ml of water is added and the mixture is heated at 50° for 15 min. The cooled soln. is washed first with 20% NaCl soln. and finally with water. The results show that the determination of benzyl alcohol is only slightly affected by the presence of benzyl benzoate. The acetylation of benzyl benzoate under the given conditions for 10 hr. yields a product containing 7% of benzyl acetate. G. R. WHALLEY

2711. **Analysis of phenol-containing volatile oils.** M. I. Blake (N. D. Agric. College, Fargo, N.D., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 400–402.—The phenol content of volatile oils was determined by non-aqueous titration, with Na methoxide in benzene - methanol as the titrant. Dimethylformamide, methyl cyanide and ethylenediamine were used as solvents and the end-points were determined potentiometrically. Analysis of 9 phenols and volatile oils containing from ≃ 20 to ≃ 100% of phenol gave results that were reproducible to within ≃ 1%. The procedure offers several advantages over the classical extraction procedure with alkali soln. G. P. COOK

2712. **Spectrophotometric determination of αβ-unsaturated aldehydes and ketones with Girard-T reagent. I. Essential oils.** J. B. Stenlake and W. D. Williams (Royal College of Sci. and Technol., Glasgow). *J. Pharm. Pharmacol.*, 1957, **9** (12), 900–907.—The results obtained by this method for the determination of citral, cinnamaldehyde or carvone in essential oils agree with those by the hydroxylamine hydrochloride method with most samples, but are lower for the determination of citral in lemon oil. The reproducibility is ≃ ± 0·5%. *Procedure*—For citral or cinnamaldehyde, reflux the sample (containing 10 to 15 mg of aldehyde) with ethanol (5 ml) and Girard-T reagent (0·2 g) for 12 min., then cool and dilute with ether (50 ml) and extract with H_2O (25 + 10 + 10 ml). Dilute the combined extracts appropriately and measure the extinction at 281 mμ (for citral, ε = 29,500) or at 313 mμ (for cinnamaldehyde, ε = 42,000) with a similarly treated blank soln. in the reference cell. For carvone, reflux the sample (containing 15 to 20 mg of ketone) with ethanol (5 ml), glacial acetic acid (0·5 ml) and Girard-T reagent (0·2 g) for 70 min. Cool. Dilute with ether (50 ml), and add sufficient *N* NaOH to

neutralise nine-tenths of the acid and obtain an aq. extract. Dilute appropriately and measure the extinction at 272·5 mμ ($\epsilon = 19{,}000$). A. R. ROGERS

2713. **Application of infra-red spectrophotometry to the examination of essential oils. I. Cineole in lavender oil.** A. H. J. Cross, A. H. Gunn and S. G. E. Stevens (Smith Kline and French Lab. Ltd., London). *J. Pharm. Pharmacol.*, 1957, **9** (12), 841–849.—Peaks of i.r. light absorption at 1310, 1220, 1085 and 885 cm^{-1} may be used for the detection of cineole in lavender oil. For quant. determination, dry the sample overnight with $MgSO_4$, prepare a 2·5% (w/v) soln. in CS_2 and obtain the spectrogram in a 0·5-mm cell, with CS_2 in a reference cell of path-length 0·485 mm; calculate the concn. of cineole by the absorbancy difference method applied to the 1085 cm^{-1} peak. The reproducibility is $\simeq \pm 2\%$. Results by the i.r. method are lower than those by the cresineol method. A. R. ROGERS

2714. **Polarographic studies of some organic compounds. V. Polarography of curcumin.** Hisashi Sato (Nat. Hyg. Lab., Tamagawa-yoga, Setagaya, Tokyo). *Japan Analyst*, 1957, **6** (9), 549–551.—Curcumin (**I**) gives a two-step wave at pH < 6 and a three-step wave at a higher pH in 80% ethanol containing 0·25 *M* NaBr, 0·04 *M* Britton-Robinson buffer and 0·028% gelatin. The reduction potential decreases with pH from 2·3 to 10·7. The wave height increases with pH and remains constant at pH > 5; it decreases with time in a soln. of pH > 7·6. The optimum condition for the determination of **I** is pH 5·2. The working curve is linear for 0·1 to 1 millimole of **I**.

VI. Polarography of fragrant aldehydes. Hisashi Sato. *Ibid.*, 1957, **6** (9), 551–556.—The polarograms of bourbonal (**II**), piperonal (**III**), cyclamen aldehyde (**IV**), salicylaldehyde (**V**) and protocatechaldehyde (**VI**) were studied in 80% ethanol containing 0·25 *M* NaBr, KI, NH_4Cl or tetramethylammonium bromide (**VII**), 0·04 *M* Britton-Robinson buffer and 0·028% gelatin, and their use for quant. analysis is discussed. The wave of those aldehydes having a free hydroxyl group in the *p*- and an alkylated hydroxyl group in the *o*-position disappears in a strongly basic soln., whilst the wave of those aldehydes having a free hydroxyl group in the *o*-position (*e.g.*, **V**) or no free hydroxyl group does not. The dependence of the polarogram (except that of **IV**) on the pH and the concn. of the aldehyde was similar to that observed for **I**. The optimum conditions for the determination of 0·1 to 1 millimole of these compounds are—**II**, pH 5·9 in KI soln., or pH 6·5 to 8·5 in **VII** soln.; **III**, pH 7·0 to 10·5 in NaBr; **IV**, pH 6·5 in **VII**; **V**, pH 3·5 to 10·5 in NaBr; **VI**, pH 5·5 to 7·0 in NaBr.

K. SAITO

2715. **Spectrographic trace analysis of textile-fibre ash after pyrrolidine[tetramethylene]dithiocarbamate - dithizone extraction.** O. G. Koch and G. A. Dedic (Neunkircher Eisenwerk A.-G., Saar). *Chemist Analyst*, 1957, **46** (4), 88, 90–91.—Ash 10 g of fibre in a platinum dish at 450°. Fuse the ash with five times its wt. of carbonate - borate flux. Dissolve the melt in 6 *M* HCl and transfer the soln. to a separating funnel. Add ammonium tartrate soln. (33% w/v) (15 ml for ≯ 60 mg of ash), and adjust the pH to 3·0 with 6 *M* aq. NH_3. Add ammonium tetramethylenedithiocarbamate or Na diethyldithiocarbamate (5% aq. soln.) (2 ml) and shake for 10 sec. Add dithizone (0·01% in $CHCl_3$) (15 ml), shake for 1 min. and separate the phases. Repeat the extraction procedure until the organic layer remains green. Repeat the extractions at pH 5·0, 7·0 and 9·0. Evaporate the combined organic layers to dryness, add beryllium soln. as an internal standard and ash at 350°. Dissolve the residue in aqua regia and evaporate to dryness. Make up to 40 μl with 6 *M* HCl and use 20 μl on each of two preheated graphite electrodes for the spectrographic analysis.

G. S. ROBERTS

2716. **The determination of total sulphur in viscose.** M. J. Maurice [N. V. Onderzoekingsinst. "Research" (A.K.U.), Arnhem, Netherlands]. *Z. anal. Chem.*, 1957, **158** (6), 410–418.—Boil a mixture of conc. HCl (160 ml), aq. HI (*d*, 1·70) (160 ml) and 50% (w/v) aq. hypophosphorous acid (45 ml) for 40 min. Heat the sample of viscose (1 g) with water (10 ml) and 50 ml of the acid mixture in a stream of N. Wash the vapours with dil. aq. H_2SO_4 and absorb the H_2S in a 0·02 *N* soln. of cupric acetate in acetic acid (50 ml) and the CS_2 in 0·1 *N* ethanolic KOH (50 ml). Determine the excess of Cu by titration with 0·02 *N* EDTA and the K ethylxanthate in the KOH soln. by its u.v. absorption at 301·5 mμ. Results by this method agree closely with those by the acidimetric method, and are about 5% higher than those by complexometric or gravimetric methods. A. R. ROGERS

2717. **Determination of lignin in bleached viscose-cellulose.** I. Slávik and L'. Kuniak (Dept. of Cellulose, Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1957, **11** (5), 285–292.—The usual methods for the determination of lignin are unreliable because some of the resinous material passes into the ppt. when the extracted sample is hydrolysed in a strongly acid medium. To determine the actual content of extractible compounds and of lignin, a new method for their separation has been suggested. *Procedure*—(*a*) Dissolve the extract (obtained from 20 g of dry cellulose) by heating in NaOH soln. (0·2%) (50 ml), cool, adjust to pH 4 with dilute acetic acid, add a soln. of $NaClO_2$ (0·2 g) and an equiv. amount of NaClO soln. Set aside for 30 min. in a stoppered flask, then add Na_2SO_3 and filter through a sintered-glass crucible G3. Dissolve the residue on the filter (resinous material) in a mixture of benzene and ethanol, dry and weigh. (*b*) Moisten 5 g of dry cellulose with H_2SO_4 (50%) (40 ml) and add carefully conc. H_2SO_4 (35 ml), keeping the temp. below 30°; cool to 20° and set aside for 2 hr. Dilute with H_2O to 700 ml, heat and set aside for 12 hr. Filter through a sintered-glass filter G4, wash, dry and weigh (lignin plus resinous material). Boil the residue with 0·2% NaOH soln., cool, oxidise and determine as described above.

J. ZÝKA

2718. **Bromine number of propylene and butylene polymers.** J. C. S. Wood (Sun Oil Co., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 372–375.—The bromine values of propylene and butylene polymers of low mol. wt. (C_6 to C_{12}) as determined by ASTM methods are 10 to 30% higher than theoretical. Investigation of the composition of such polymers shows that they consist substantially of aliphatic mono-olefins. Elimination of the $HgCl_2$ catalyst in the titration solvent of the ASTM electrometric method (D1159–55T) gives results which agree with theoretical values. A maximum deviation of + 6 was obtained in the bromine value range of $\simeq$ 120 to 200; the unmodified procedure gave a max. deviation of + 21.

Additional data suggest that the modified method is also more accurate for the olefin types that normally occur in cracked petrols. G. P. Cook

2719. **The determination of lead in poly(vinyl chloride) compositions containing lead stabilisers.** S. Grossman and J. Haslam (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *J. Appl. Chem.*, 1957, **7** (11), 639–644.—In the rapid procedure described, the sample (0·25 g) is dissolved in 1:2-dichloroethane (50 ml), and the Pb is removed from this soln. by two extractions into conc. HCl. The acid phase is separated, diluted to $\simeq$ 50% HCl (v/v) with H_2O, and the u.v. extinction of the $PbCl_2$ complex is measured at 270 mμ in a 1-cm cell against a blank. The percentage of Pb is determined from the standard curve (0 to 1·2 mg of Pb per 100 ml of soln.). If Fe is present the extinction is measured at 270 mμ and 340 mμ (Fe alone), and a correction is made for the extinction caused by Fe at 270 mμ. Values between 2 and 6% of Pb agree well with the longer gravimetric method, even when Ti, Ca, Si or Sn is present. W. J. Baker

2720. **Determination of alpha-glycol content of epoxy resins.** G. A. Stenmark (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 381–383.—The periodate method for the determination of α-glycol groups was applied to epoxy resins, $CHCl_3$ being used as the solvent and an alcoholic soln. of a quaternary ammonium periodate as the reagent. The method gives accurate results with pure glycols and is sensitive to low concn. of glycols in epoxy resins. Other functional groups, including epoxy and phenolic groups, do not interfere. G. P. Cook

2721. **Analytical chemistry related to urea resins. IV. Determination of mono- and di-(hydroxymethyl)urea in an initial condensation mixture by means of infra-red absorption spectroscopy.** Shigeyuki Tanaka, Masayuki Ogawa, Yasuo Miyamoto and Naoyoshi Yoshimi (Inst. of Techno-anal. Chem., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1957, **6** (9), 562–564.—Mono- (**I**) and di-(hydroxymethyl)urea (**II**) have absorption max. at 9·87 and 9·53 μ, respectively (potassium bromide pellet method), whereas urea has no absorption in this region. Since the extinction of **I** and **II** increases linearly with concn. ($<$ 0·3 mg per 500 mg of KBr), they can be determined by the use of these two peaks as key bands. The standard deviation is $\simeq \pm$ 1·7%. A reaction mixture in hexamine is dried in a vacuum desiccator (for $\simeq$ 2 days), after the removal of hexamine by extraction (*Anal. Abstr.*, 1956, **3**, 3123), and mixed with KBr. No change in the content of the CH_2OH radical was observed during storage in a desiccator. K. Saito

2722. **Precipitation titration of N-methoxymethyl-ϵ-caprolactam polymers.** J. Majer and O. Peroutka (Res. Inst. Macromol. Chem., Brno, Czechoslovakia). *Chem. Průmysl*, 1957, **7** (11), 617–619.—The method is based on the pptn. of the polymer from aq. ethanolic soln. by addition of water or acetone. When the initial vol. of soln. is kept constant, the vol. of precipitant added is linearly dependent on the degree of substitution and is only slightly dependent on polymer concn. J. Böswart

2723. **Photometric determination of zinc oxide in rubber products. Absorptiometric and turbidimetric methods using sodium diethyldithiocarbamate.** K. E. Kress (The Firestone Tire and Rubber Co., Akron, Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 432–440.—The sample (1 to 15 mg) is either dry-ashed at $\simeq$ 550° or, preferably, wet-ashed with conc. HNO_3 and 70% $HClO_4$ in a borosilicate tube. The Zn is then pptd. from weakly alkaline soln. (aq. NH_3) as Zn diethyldithiocarbamate. The ppt. can either be extracted with diethyl ether and the extinction of the complex measured at 262, 280 or 295 mμ (according to wt. of sample) or converted into a colloidal aq. suspension, the transmission of which is measured at 448 mμ against H_2O as blank. The turbidimetric method is suitable for routine use, but the absorptiometric method is more sensitive and enables interfering cations (Co, Cu, Ni, Fe) to be detected and corrected for. For concn. of 0·2 to 3·5 p.p.m. of Zn, 40 ml of ether soln. are taken, but for concn. $<$ 0·05 p.p.m. the vol. is reduced to 5 or 10 ml. The concn. at which Cu, Co, Ni, Mn, Fe, Pb, Ba or Ca interferes with recovery of 10 p.p.m. of Zn in the turbidimetric method are listed; this method is invalid for samples containing much $CaCO_3$ or $BaCO_3$. For ZnO contents of 1 to 4%, precision and accuracy of both methods equate with those of the usual volumetric method. The treatment of special samples is described. W. J. Baker

---

See also Abstracts—**2486**, Prep. of Bindschedler's green. **2503**, Titrations of aprotic acids. **2540**, Determination of Ca and Ag in photographic materials. **2587**, Colour test for organic nitrates. **2734**, Determination of primary amino groups. **2822**, Separation of phenols by column chromatography. **2825**, Use of cellulose ester paper in chromatography. **2829**, Apparatus for vapour-phase chromatography. **2856**, Determination of organic compounds by chronopotentiometry.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2724. **Validity of the urea method for estimating total body-water in malnutrition.** S. G. Srikantia and C. Gopalan (Nutrition Res. Lab., Indian Council Med. Res., Coonoor, S. India). *Lancet*, 1957, **ii**, 1037.—Total body-water was determined in five normal adults and five malnourished oedematous patients. The differences in the results obtained by the urea and phenazone methods were small and no greater in the patients than in the normal people. These results indicate that the urea method is suitable for the determination of total body-water even in malnourished patients.

2725. **New chromatographic method for the determination of barbiturates.** K. Kácl (Lab. of Toxicol. and Forensic Med., Prague). *Soudní Lékařství*, 1957, **2** (2), 17–19.—Urine containing barbiturates is extracted with ether (2 $\times$ 10 ml), the extract is evaporated with a few drops of ethanol, the residue is dissolved in ethanol and placed on Whatman No. 1 paper. A mixture of amyl alcohol and aq. NH_3 (10%) (2:1) is used for chromatography. The chromatogram is photographed on reflectographic paper at 254 mμ and the same procedure is repeated with the chromatogram

moistened with 0·5 *N* NaOH. Spots due to barbiturates change their position. As little as 10 to 25 μg of barbiturate in 1 to 10 ml of urine can thus be detected. J. ZÝKA

2726. **Analytical studies on fluoride. III. Colorimetric determination of fluoride in animal tissue with the thorium - neothorin reagent.** Koichi Emi and Tadashi Hayakawa (Fac. of Sci., Okayama Univ., Tsushima). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (10), 1532–1534.—A small amount of F^- (1 to 200 μg) in animal tissue can be satisfactorily determined in the ash obtained by calcination with CaO (15 to 20% by weight of the dry sample). The sample mixed with CaO is charred at 350° to 450° and ignited at 700° to 750° for 30 min. (recovery of F, ≃ 99%). The residue is decomposed with H_2SO_4 and the F^- are distilled and colorimetrically determined with a mixture of Th^{4+} and neothorin [*o*-(1:8-dihydroxy-3:6-disulpho-7-naphthylazo)benzenearsonic acid] as described previously (*Anal. Abstr.*, 1956, **3**, 2475; 1957, **4**, 3159). K. SAITO

2727. **Determination of galactose in small amounts of blood.** H. M. C. Robinson and J. C. Rathbun (Dept. of Pediatrics, Univ. of W. Ontario, London, Canada). *Canad. J. Biochem. Physiol.*, 1957, **35** (11), 935–943.—Protein is pptd. from heparinised blood (0·1 ml) by isotonic tungstate and H_2SO_4. The filtrate is treated with yeast to ferment glucose and the galactose is then determined colorimetrically at 680 mμ with modified Somogyi and Nelson reagents. H. F. W. KIRKPATRICK

2728. **Enzymic method for the determination of formic acid.** J. C. Rabinowitz and W. E. Pricer, jun. (Nat. Inst. of Arthritis and Metabolic Diseases, Nat. Inst. of Health, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1957, **229** (1), 321–328.—A specific spectrophotometric method is described, in which an enzyme prep. from lyophilised cells of *Clostridium cylindrosporum* is used. The method is based on the enzymic conversion of formic acid into 10-formyltetrahydrofolic acid, and spectrophotometric determination, at 350 mμ, of the 5:10-methenyltetrahydrofolic acid, which is formed by the action of acid on the enzymic reaction product. Formic acid can be determined directly in biological samples that contain 0·02 to 0·2 μmole of the acid per ml. J. N. ASHLEY

2729. **Chemical estimation of adrenaline and noradrenaline in human and canine plasma. II. Critique of the trihydroxyindole method.** H. L. Price and M. L. Price (Pennsylvania Univ. Hosp., Philadelphia, U.S.A.). *J. Lab. Clin. Med.*, 1957, **50** (5), 769–777.—The fluorimetric method described is suitable for determining 1 mμg of adrenaline (**I**) and 2 to 3 mμg of noradrenaline (**II**). After preliminary chromatography on alumina, fluorescence is developed by treatment with $K_3Fe(CN)_6$ followed by ascorbic acid and aq. NaOH. The fluorescence is measured with exciting radiation of wavelengths 400 and 436 mμ, and the amounts of **I** and **II** are calculated by the method given. In the series of biologically occurring substances examined, only *iso*propylnoradrenaline interfered; this could be distinguished from **I** but not from **II**. The concn. of **I** and **II** in normal human plasma were ≃ 0·10 and 0·20 μg, respectively. W. H. C. SHAW

2730. **Assay of glucagon and epinephrine [adrenaline] with use of liver homogenates.** J. Berthet, E. W. Sutherland and T. W. Rall (Dept. of Pharmacol., Sch. of Med., Western Reserve Univ., Cleveland, Ohio, U.S.A.). *J. Biol. Chem.*, 1957, **229** (1), 351–361.—Conditions are given for the assay of glucagon and sympathomimetic amines by means of a dog-liver homogenate. This responds to the presence of glucagon and adrenaline, etc., by an increase in the formation of phosphorylase from dephosphophosphorylase, and the phosphorylase activity is then measured by a standard method. The inherent accuracy of the homogenate assay system is about four times as great as that of the liver-slice method. Addition of insulin or casein increases the sensitivity of the method to glucagon but not to adrenaline, whereas addition of caffeine increases the sensitivity towards both compounds. Ergotamine inhibits the response of the system to adrenaline but not to glucagon. The method is applicable to purified glucagon or purified pancreatic extracts, but the determination of glucagon in blood is limited by the presence of interfering substances. J. N. ASHLEY

2731. **The estimation of physiologically active, naturally occurring substances in the tissues and body fluids: acetylcholine, (−)-adrenaline, (−)-noradrenaline, histamine, serotonin and substance P. IV. Histamine.** J. J. Lewis and N. G. Waton (Dept. Materia Medica and Therapeutics, Glasgow Univ.). *Lab. Practice*, 1957, **6** (11), 649–652.—The importance of and methods for the extraction, protein precipitation, and purification by paper chromatography are reviewed. Paper chromatography can be used as an approximate quantitative technique. D. P. FELIX

2732. **Detection of purines and pyrimidines on paper chromatograms.** N. Pfennig (Inst. für Mikrobiol., Univ., Göttingen). *Naturwissenschaften*, 1957, **44** (20), 537.—Purine and pyrimidine bases are usually located on paper chromatograms by examination in u.v. light when they show as dark spots on a faintly fluorescent background. This background fluorescence can be greatly enhanced by adding a fluorescent substance to the developer. The only fluorescent substance which was found to move faster than any of the purines and pyrimidines in the developer *iso*propyl alcohol - 2 *N* HCl (65:35) was aesculin. Not more than 6 to 12 mg of aesculin need be added to 100 ml of the developer to give the paper an intense light-blue fluorescence, against which the purines and pyrimidines stand out as dark areas. When examined at 275 mμ, guanine alone shows an intense violet fluorescence. The guanine fluorescence and all spots appear much weaker when the paper is examined at 231 mμ. E. KAWERAU

2733. **Thyrotrophin assay by plasma ^{131}I measurements.** D. D. Adams and H. D. Purves (Med. School, Dunedin, N. Zealand). *Canad. J. Biochem. Physiol.*, 1957, **35** (11), 993–1004.—The assay depends on the increase in concn. of ^{131}I in the plasma of thyroxine-treated guinea-pigs produced by injection of thyrotrophin. The method is essentially that previously described (*Endocrinology*, 1955, **57**, 17), but a modified design is suggested as a result of a further study of the dose - response relationship. H. F. W. KIRKPATRICK

2734. **Modified Van Slyke method.** F. Péter (Dept. of Org. Chem. Technol., Technol. Univ., Budapest). *Magyar Kém. Foly.*, 1957, **63** (10), 289–293.—A dynamic gas-volumetric method for the determination of primary amino-groups is described in detail. The experimental conditions are based on Van Slyke's method, but the new

method is claimed to be simpler, quicker, more accurate and to require less preliminary work. It is suitable for the examination of many types of compound containing primary amino-groups.
A. G. PETO

2735. **Quantitative evaluation of paper chromatograms [of amino acids] by the Zeiss leucometer (preliminary communication).** S. Szőke and L. Szalai (Res. Inst. for Cereals and Flour, Budapest). *Acta Chim. Acad. Sci. Hung.*, 1957, **12** (3-4), 295–297 (in English).—The Zeiss leucometer is used for the quant. analysis of amino acids in protein hydrolysates after separation by paper chromatography. The spots are treated with ninhydrin reagent and measured with the use of a green filter; the difference between the reflection of a spot and of untreated paper is a linear function of the logarithm of the concn. of amino acid.
A. R. ROGERS

2736. **Proteins. XLIII. Isolation of dinitrophenyl derivatives of amino acids and peptides by ion exchange.** B. Keil (Chem. Inst., Biochem. Dept., Acad. Sci., Prague). *Chem. Listy*, 1957, **51** (10), 1927–1931.—It has been found that the dinitrophenyl derivatives of amino acids and peptides can be separated from free amino acids and peptides on a basic ion exchanger. A procedure for the preparation and isolation of dinitrophenyl derivatives on the micro scale has been developed and confirmed with synthetic peptides and peptides prepared from partially hydrolysed chymotrypsinogen. With the use of ion exchange and paper electrophoresis a selective separation of a peptide fraction containing arginine is possible. J. ŽÝKA

2737. **Decarboxylation of amino acids, proteins and peptides by N-bromosuccinimide.** E. W. Chappelle and J. M. Luck (Dept. of Chem., Stanford Univ., Calif., U.S.A.). *J. Biol. Chem.*, 1957, **229** (1), 171–179.—A method is described for the determination of amino acids and of end carboxyl groups in peptides and proteins by reaction with aq. N-bromosuccinimide in the presence of *M* Na acetate - acetic acid buffer at pH 4·7 and 30°. The carboxyl group is quant. eliminated as CO_2, which is measured manometrically in the Warburg apparatus. The rate of reaction, for peptides and proteins, is increased by the addition of $PdCl_2$ to the reaction mixture. The reaction is specific for carboxyl groups adjacent to an α-substituted C atom. Aspartic acid affords 2 moles of CO_2 per mole of acid and β-alanine reacts only very slowly.
J. N. ASHLEY

2738. **Differentiation of α-amino acids and amines by non-enzymatic transamination on paper chromatograms.** G. D. Kalyankar and E. E. Snell (Dept. of Biochem., Univ. of California, Berkeley, U.S.A.). *Nature*, 1957, **180**, 1069–1070.—After transamination with pyridoxal, α-amino acids can be distinguished from β-amino acids and other primary amines by redevelopment of chromatograms with ninhydrin. *Procedure*—Run duplicate chromatograms by the ascending technique with a mixture of *n*-butanol - acetic acid - water (4:1:5) (upper layer) as solvent. Dry the papers in air, spray one with a soln. of pyridoxal hydrochloride [0·25% in ethanol (95%) adjusted to pH 5·5], and re-dry. Heat the chromatograms at 90° for 10 min., spray both with ninhydrin soln. (0·25% in acetone) and dry them at room temp., or heat at 90° for 5 min. Purple spots due to α-amino acids (and benzylamine) turn orange with both treatments, and β-acids show negligible colour change after heat treatment at 90°. Individual acids can be identified in some cases by examination of the chromatograms in u.v. light.
D. G. FORBES

2739. **Fluorimetric method for the estimation of tyrosine in plasma and tissues.** T. P. Waalkes and S. Udenfriend (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Lab. Clin. Med.*, 1957, **50** (5), 733–736.—The method is based on the reaction of tyrosine with 1-nitroso-2-naphthol and measurement of the fluorescence of the derivative. The specificity and sensitivity of the procedure and its application to human plasma are discussed. *Procedure*—Dilute 1 ml of plasma sample with 4 ml of water and add 1 ml of 30% trichloroacetic acid soln. Centrifuge after 10 min. To 2 ml of the supernatant liquid in a glass stoppered centrifuge tube add 1 ml of 0·1% 1-nitroso-2-naphthol in ethanol (95%) and 1 ml of HNO_3 reagent [24·5 ml of HNO_3 (1:5) mixed with 0·5 ml of 2·5% $NaNO_2$ soln.]. Close the tube, shake and heat in a water bath at 55° for 30 min. Cool, add 10 ml of 1:2-dichloroethane and shake. Centrifuge and read the fluorescence of the supernatant liquid at 570 mμ under activation with 460 mμ radiation.
W. H. C. SHAW

2740. **Determination of histamine and histidine in bacterial cultures.** A. S. Issaly, F. C. Pennimpede and I. S. M. de Issaly. *Rev. Asoc. Bioquim. Argentina*, 1957, **22**, 67–71.—Histamine is separated from histidine and iminazoles by adsorption on Permutit and subsequent elution by NaCl soln. The histamine and histidine contents of the two fractions are determined by reaction with diazotised sulphanilic acid and measurement of the colour formed. A Klett - Summerson photometer is used, with filter No. 54.
G. H. FOXLEY

2741. **The separation of free alanine, glycine, histidine, arginine, lysine, ornithine and "fast arginine" from blood serum by means of paper electrophoresis.** G. Donovan, M. Solomon and I. Stăncescu (Lab. Exp. Physiol., Inst. Pădiatrie, Bucharest). *Rev. Chim., Romania*, 1957, **2** (2), 305–312 (in German).—After a review of previous work on the separation of amino acids by paper chromatography and electrophoresis, a method is described which permits the complete separation of the acids cited above from blood serum. This is achieved by carrying out paper electrophoresis at a relatively low voltage (17·5 V per cm) on a long (56 cm) paper strip, which is slowly unrolled in the cathode compartment and rewound in the anode compartment to give an effective length of 45 cm. The amino-acid fraction used is separated from blood serum by a complicated purification process, which is described. The electrophoresis, which lasts for 3 hr. 45 min., is carried out in a medium (pH 1·9) which consists of a mixture of 2 *N* glacial acetic acid and 0·6 *N* formic acid. The strip is dried for 15 min. at 90° and developed with a soln. of ninhydrin in acetone. Distinct and separate blue - violet bands appear, which can be fixed as red or red - gold complexes by spraying with copper nitrate in acetone. Only very small amounts of peptides are carried over from the blood serum, and the neutral and acid amino acids, which do not migrate under the conditions employed, remain behind alanine on the electropherogram. The apparatus is shown diagrammatically and results obtained for human and canine blood serum are illustrated. The method is simple and could possibly be applied to routine tests.
S. M. MARSH

2742. **A new micro-determination of the total quantity of cysteine plus cystine in protein by hydrazinolysis.** Kazuoki Kuratomi, Ko Ohno and Shiro Akabori (Osaka Univ.). *J. Biochem., Tokyo*, 1957, **44**, 183–190.—A simplified method has been devised for the micro-determination of the sum of L-cystine (**I**) and of L-cysteine (**II**) in protein. *Procedure*—Mix the protein sample, containing a total of 10 to 15 μmoles of **I** and **II**, with 0·5 ml of hydrazine hydrate, heat at 115° to 120° for 5 to 7 hr. in a hydrazinolysing apparatus equipped with a condenser and a glass delivery tube. Cool, dilute to a vol. of 4 to 5 ml, add 10 ml of 6 *N* H_2SO_4 drop by drop, heat at 50° to 55° in a current of N (2·4 to 3 litres per hour) for 30 min., passing the liberated H_2S into 5·0 ml of Zn acetate reagent (60 g of Zn acetate, 17 g of Na acetate and 0·05 g of NaCl per litre). Add 5·0 ml of 0·05% dimethyl-*p*-phenylenediamine soln. containing 20 ml of conc. H_2SO_4 per 100 ml, and then 1·0 ml of 12·4% ferric ammonium sulphate soln. containing 2·52 ml of conc. H_2SO_4 per 100 ml. Set aside for 1 hr., dilute 5 to 10-fold, and determine the extinction coeff. at 630 mμ. For the standard soln. use 25 μmoles of **I**. The error ranges from + 3 to − 2% with 12·5 to 25·5 μmoles of **I** or **II**. The recovery with the use of 25 μmoles of **I** or **II** is 98 to 100% even in the presence of methionine, tyrosine, proline, histidine or phenylalanine. The amounts of **I** in lysozyme and half-cystine in ovalbumin, respectively, are 4·93 to 5·08 and 7·33 to 7·55 μmoles per mole. CHEM. ABSTR.

2743. **Quantitative muscle-protein determination.** E. Helander (Inst. of Anatomy, Univ. of Gothenburg, Sweden). *Acta Physiol. Scand.*, 1957, **41**, Suppl. 141, 99 pp. (in English).—Optimum conditions are defined for quant. protein extraction from skeletal muscle. A method is given for the separate determination of sarcoplasm, myofibril and stroma proteins. H. F. W. KIRKPATRICK

2744. **Practical observations on the total fractionation of blood proteins.** J. F. Frattini (División de Higiene y Medicina Preventiva, Sanidad Militar, Argentina). *Rev. Asoc. Bioquim. Argentina*, 1957, **22**, 201–210.—Replacement of diethyl ether by $CHCl_3$ is recommended for the separation of albumin in blood serum by treatment with 27% Na_2SO_4 (anhyd.) soln. followed by centrifuging. The amounts of α-, β- and γ-globulins, albumin and fibrinogen in blood serum can be obtained by fractional pptn. from serum by Na_2SO_4 soln. of various concn. The use of graphs indicating the amounts of albumin and α-, β- and γ-globulins in serum is suggested. G. H. FOXLEY

2745. **The identification of nucleic acids in blood proteins.** J. Rechenberger (Med. Univ.-klinik, Leipzig, Johannisallee 32). *Naturwissenschaften*, 1957, **44** (18), 494–495.—The protein of plasma or serum (0·5 ml) is pptd. by the addition of excess of methanol, the ppt. is washed several times with methanol, and hydrolysed for a short time at 37° with either 0·9% NaCl soln. or 0·1 *N* NaOH. The ppt. is then extracted, first in the cold with 5% $HClO_4$ and then at 80° for 5 min. with 20% $HClO_4$. The extracts are combined and centrifuged, and the extinction curve of the supernatant liquid is plotted with the aid of a u.v. spectrophotometer over the range 240 to 310 mμ. The extinction curves have maxima at 260 and 266 mμ, which coincide with the absorption maxima of pure ribonucleic acid. The $HClO_4$ extracts were also analysed chemically for their respective ribonucleic and deoxyribonucleic acid contents by direct determination of both ribose and deoxyribose, the ribose by the orcinol reaction, the deoxyribose by the indole reaction. These quant. determinations have shown that often more than 90% of the nucleic acid is present as ribonucleic acid. Data from six pathological cases are presented. E. KAWERAU

2746. **New turbidimetric method for the determination of γ-globulin.** J. F. Frattini (División de Higiene y Medicina Preventiva, Sanidad Militar, Argentina). *Rev. Asoc. Bioquim. Argentina*, 1957, **22**, 211–216.—Blood serum is treated with stabilised $HgCl_2$ soln. and the turbidity of the mixture is measured photo-electrically. A standard $BaSO_4$ suspension is used for calibration purposes, and a formula is given to convert turbidity units to γ-globulin (%). Results are given for 19 samples analysed by the proposed method and also by the biuret, Huerga and Popper, Kunkel, and electrophoresis methods. G. H. FOXLEY

2747. **Direct method for the determination of total cholesterol in serum.** J. F. Torres. *Rev. Asoc. Bioquim. Argentina*, 1957, **22**, 28–33.—The colour obtained by treating cholesterol with Co^{2+} in acetic acid - H_2SO_4 medium obeys the Beer - Lambert law and has maximum absorption at 500 mμ. *Reagent*—Dissolve 85·5 mg of $CoCl_2.5H_2O$ in 2 ml of double-distilled water, add 5 ml of glacial acetic acid and make up to 100 ml with conc. H_2SO_4 (*d* 1·84). *Procedure*—Mix 0·1 ml of serum with 6 ml of glacial acetic acid and add 4 ml of reagent. Measure the extinction at 500 mμ and calculate the cholesterol by reference to a calibration curve. Cholesteryl esters can also be determined by this method and recovery is 98 to 100%. The colour given by proteins can be ignored. Results are in good agreement with those obtained by other methods. G. H. FOXLEY

2748. **Paper chromatography and colorimetric determination of free and esterified cholesterol in very small amounts of blood.** P. W. Hansen and H. Dam (Polytech. Inst., Copenhagen, Denmark). *Acta Chem. Scand.*, 1957, **11** (10), 1658–1662.—The Zlatkis colour reaction (*cf. J. Lab. Clin. Med.*, 1953, **41**, 486), which is unreliable with whole serum, is satisfactory when applied to cholesterol and its esters separated by paper chromatography from blood serum, so that 2·5 μg can be determined to within ± 5%. *Procedure*—Plasma (0·02 ml) is mixed with 0·3 ml of acetone - ethanol (1 : 1), heated to between 80° and 85° for 5 min., shaken violently for 1 min. and centrifuged. The supernatant liquid and subsequent washings of the ppt. are transferred to a paper cut to give 8 independent strips. One strip is left as a blank. The chromatogram is run upwards with *iso*octane as the mobile phase for 20 min. (front travels 10 cm). The position of the spots is detected on one of the strips and the corresponding positions on the others are extracted with 1 ml of $CHCl_3$. The $CHCl_3$ extracts are evaporated and the residues treated with 0·20 ml of Zlatkis reagent (0·5 ml of a soln. containing 1 g of $FeCl_3$ in 10 ml of acetic acid mixed immediately before use with 25 ml of conc. H_2SO_4). The reagent and residue are rapidly mixed with a small glass rod, placed on a boiling-water bath for exactly 1 min., cooled to room temp., and the absorption measured at 530 mμ. Cholesterol, cholesteryl acetate and cholesteryl palmitate give identical absorptions for equivalent amounts. E. J. H. BIRCH

2749. **Polarographic estimation of formaldehydogenic and acetaldehydogenic steroids.** L. Stárka (Res. Inst. of Endocrinology, Prague). *Naturwissenschaften*, 1957, **44** (22), 585 (in English).—Both formaldehyde and acetaldehyde have well-developed cathodic waves (in 0·1 *N* LiOH) with $E_{\frac{1}{2}}$ of 1·63 and 1·77 V, respectively, and the dependence of limiting current on concn. is linear. With normal polarographic equipment, 5 μg of aldehyde can be determined and, with a micro-polarograph and working at higher temperatures, 0·5 μg of aldehyde can be determined with an error of 5%. The steroids are extracted in the customary manner and the aldehyde is produced by oxidation with HIO_4 in acid soln. Preference is given to the following method which avoids distillation of the aldehyde. After being set aside for 1 hr. the oxidation mixture is reduced by addition of 0·4 *M* lithium bisulphite, made alkaline with lithium hydroxide and the polarographic wave is recorded. The beginning of the formaldehyde wave is frequently deformed. E. Kawerau

2750. **Rapid method for purification and determination of progesterone from luteal tissue.** R. G. Loy, W. H. McShan and L. E. Casida (Univ. of Wisconsin, Madison, U.S.A.). *J. Biol. Chem.*, 1957, **229** (2), 583–588.—The determination of progesterone from sow and cow luteal tissue is based on adsorption chromatography on columns of Al_2O_3, counter-current distribution between light petroleum (boiling range 30° to 60°) - 70% methanol, and spectrophotometric determination at 240 mμ. The extraction and determination require only 7 to 8 hr., and the method may be applicable, with appropriate modification, to the analysis of body fluids for progesterone. J. N. Ashley

2751. **Critical analysis of methods for measurement of pregnane-3α:17α:20α-triol in human urine.** A. M. Bongiovanni and W. R. Eberlein (Univ. Pennsylvania, Philadelphia, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 388–393.—Three methods, one based on the colour produced by H_2SO_4 after chromatography and two depending on the production of acetaldehyde or 17-oxosteroids after oxidation with periodate or chromic acid, respectively, are critically compared. Close agreement between the H_2SO_4 chromogen method and the IO_4^- oxidation procedure was obtained; the chromic acid oxidation method gave uniformly high results owing to the production of 17-oxosteroids from precursors other than the pregnanetriol. Ten specimens of urine containing 0·3 to 20 μg per ml were analysed by the H_2SO_4 chromogen procedure and gave an average difference of 1·3% between duplicates. Results also show that the IO_4^- procedure without preliminary chromatography may prove satisfactory for determining pregnanetriol. G. P. Cook

2752. **Measurement of enzymic amylolytic activity. Group B. I. Chemical methods.** H. Wildner and G. Wildner (Ireks Forschungsinst. für Gärungswissenschaft, Kulmbach, Germany). *Brauwissenschaft*, 1957, **10** (10), 255–260; (11), 285–290.—Detailed descriptions are given of published methods for the determination of amylolytic activity in blood, kidney, liver and pancreas, and malt, flour, honey, and bakery and textile extracts. P. S. Arup

2753. **Laboratory determination of pepsin in gastric juice with radioactive iodinated albumin.** A. P. Klotz and M. R. Duvall (Kansas Univ. Med. Center, Kansas City, U.S.A.). *J. Lab. Clin. Med.*, 1957, **50** (5), 753–757.—Albumin, labelled with ^{131}I and of known specific activity, is diluted with bovine albumin as carrier and the mixture is adjusted to pH 2 with Sørensen's buffer. Clear centrifuged gastric juice (1 ml) is added and the mixture is incubated at 37° for 15 min. Trichloroacetic acid is then added and the resulting ppt. is removed by centrifugation. The clear supernatant liquid, the wash liquor and the ppt. dissolved in aq. NaOH are all counted in a scintillation counter, and the percentage activity remaining in the supernatant fluids is calculated. A standard curve is prepared with 0·1 to 5·0 mg of cryst. pepsin, and the activity of the sample is read directly from the curve. W. H. C. Shaw

---

See also Abstracts—**2545**, Determination of Zn in biological material. **2563**, Determination of ^{14}C. **2625**, Determination of F^- in tooth enamel. **2758**, Determination of ketosteroids. **2768**, Determination of choline esters. **2824**, Chromatographic separation of nucleotides. **2825**, Use of cellulose ester paper in chromatography. **2830**, Apparatus for CO_2 in expired air.

Drugs

2754. **The determination of morphine in opium and some of its galenical preparations.** D. C. Garratt, C. A. Johnson and C. J. Lloyd (Standards Department, Boots Pure Drug Co. Ltd., Nottingham). *J. Pharm. Pharmacol.*, 1957, **9** (12), 914–928.—The method for the determination of morphine (**I**) in opium that depends on pptn. of the dinitrophenyl ether with 1-fluoro-2:4-dinitrobenzene (**II**) has been critically examined, with special reference to the method of washing and drying the ppt. The following procedure describes the determination of **I** in Turkish opium; modifications of the method permit determination of **I** in Indian opium, tincture, camphorated tincture, dry extract, and liniment of opium, ipecacuanha and opium powder, papaveretum (and injection and tablets) and liquid extract of poppy. Results for the determination of **I** in Turkish opium show good agreement with those by the United Nations method; the range of 15 replicates was < 2%. *Procedure*—Triturate the powdered sample (1 g) with 95% ethanol - aq. NH_3 (3:1) (4 ml). Gradually add Al_2O_3 with trituration until a free-flowing powder is obtained. Transfer to a chromatographic tube (40 cm × 1·5 cm) and elute with $CHCl_3$ - *iso*propyl alcohol (3:1) (100 ml) at about 1·5 ml per min. Extract the eluate with 0·1 *N* NaOH (20 + 15 + 15 ml). Strain the bulked aq. extracts through cotton wool, acidify with *N* HCl, and concentrate on a steam bath to 30 ml. Cool; add a 0·8% soln. of **II** in acetone (30 ml) and aq. NH_3 (5 ml). After 4 hr., transfer the ppt. to a sintered-glass crucible (porosity 3), wash with acetone (4 × 2 ml), dry at 80° for 1 hr. and weigh. A. R. Rogers

2755. **Determination of papaverine and narcotine by using ammonium reineckate.** Lee Kum Tatt and C. G. Farmilo (Food and Drug Directorate, Ottawa, Canada). *Nature*, 1957, **180**, 1288–1289.—A soln. of papaverine and narcotine in $CHCl_3$ is shaken mechanically for 30 min. with 0·1 *N* HCl and 2% aq. ammonium reineckate, and filtered through a fritted glass filter of medium porosity. Papaverine reineckate remains on the filter and is determined colorimetrically at 525 mμ. The red

$CHCl_3$ layer in the filtrate is separated from the aq. layer, and shaken with 1% aq. $AgNO_3$ soln. The clear $CHCl_3$ layer is evaporated, yielding colourless crystals of narcotine, which is determined by non-aqueous titration in acetic acid with $HClO_4$, with crystal violet as indicator. Recovery of the two alkaloids from known mixtures was satisfactory, and the procedure, when applied to opium, gave results slightly higher than those by the method of Anneler (*Arch. Pharm., Berlin*, 1920, **258**, 130).

R. E. Essery

2756. **The use of oxidised cellulose for the determination of strychnine in pharmaceutical preparations.** D. A. Elvidge and K. A. Proctor (Standards Dept., Boots Pure Drug Co. Ltd., Nottingham). *J. Pharm. Pharmacol.*, 1957, **9** (12), 974–982.—Strychnine (**I**) can be separated from extraneous interfering materials, but not from brucine (**II**), by use of oxidised cellulose as a cation-exchange medium. Preliminary purification of the sample may be necessary. **I** and **II** are then determined spectrophotometrically. The coeff. of variation is $\simeq \pm 1\%$. Results agree well with those by chemical assay. It is shown that the oxidation stage in the B.P. assay of nux vomica completely destroys **II** with no loss of **I**. *Procedure*—For tablets or pills, extract the powdered sample with 70% ethanol (50 to 100 ml) and purify by passage through a column of alumina (20 g). For mixture of potassium bromide and nux vomica or compound bismuth mixture with pepsin, make alkaline with aq. NH_3 and extract with $CHCl_3$ (4×20 ml); wash the extracts with H_2O (10 ml) and use the bulked $CHCl_3$ extracts. For extracts or tincture of nux vomica, prepare a soln. in ethanol. For prepared nux vomica, extract the finely powdered sample with 70% ethanol. Transfer an aliquot of the soln. or extract, containing 0·5 mg of **I**, to a 1-g column of oxidised cellulose of 16 to 22% carboxylic content and adjust the rate of flow to about 3 ml per min. Wash with H_2O until the eluate (in a 1-cm cell) shows an extinction $< 0{\cdot}005$ at 250 mμ. If purification by $CHCl_3$ extraction has been used, pass ethanol (10 ml) through the column before the H_2O; with samples of prepared nux vomica, wash the column with ethanol (10 ml), $CHCl_3$ (50 ml), ethanol (10 ml) and H_2O (50 ml) in succession. Elute **I** and **II** from the column with *N* H_2SO_4 and collect 50 ml. If **I** and **II** are present together, measure the extinction at 262 mμ and at 300 mμ; the values of $E^{1\%}_{1cm}$ at 262 mμ and 300 mμ are, respectively, 322 and 5·16 for **I**, and 312 and 216 for **II**. If **II** is absent, measure the extinction at 254 mμ; $E^{1\%}_{1cm}$ for **I** is 375.

A. R. Rogers

2757. **Separation of glycosides of the red foxglove (*Digitalis purpurea* L.) by paper chromatography.** C. Günzel (Pharm. Inst., Humboldt Univ., Berlin, Germany). *Z. anal. Chem.*, 1957, **159** (1), 36.—A satisfactory separation of gitaloxin from admixture with digitoxin, gitoxin and the purpurea glycosides *A* and *B* is made when a mixture of methanol, $CHCl_3$ and H_2O (1:1:1 by vol.) is used as solvent. Gitaloxin shows up blue to blue-green in visible light when treated with anisaldehyde-glacial acetic acid-H_2SO_4 reagent, and fluoresces bright blue in u.v. light. The solvent has proved suitable in the chromatographic investigation of leaf extracts.

J. H. Waton

2758. **Spectrophotometric determination of αβ-unsaturated aldehydes and ketones with Girard-T reagent. II. Ketosteroids.** J. B. Stenlake and W. D. Williams (Royal College of Sci. and Technol., Glasgow). *J. Pharm. Pharmacol.*, 1957, **9** (12), 908–913.—The results of this rapid method for the determination of ethisterone (**I**) or methyltestosterone (**II**) in tablets show reasonable agreement in most cases with those by the U.S.P. XV continuous extraction method. *Procedure*—Heat the powdered sample (containing about 10 mg of ketosteroid) with glacial acetic acid (10 ml, used in portions) on a bath of boiling water for 2 min., cool and filter. Extract the residue with glacial acetic acid (3 ml) as before, cool and filter; use part of the filtrate to dilute the other combined extracts to 10 ml, and reserve the remainder for preparation of a blank soln. To a 1-ml aliquot of the combined extracts add Girard-T reagent (20 mg), heat on a bath of boiling water for 3 min., cool, and immediately add sufficient NaOH soln. to neutralise nine-tenths of the acid. Dilute with H_2O to 200 ml and measure the extinction at 282 mμ (for **I**) or at 283 mμ (for **II**) in 1-cm cells; for a blank use 1 ml of the reserved portion treated in the same way. If it is known that the tablet basis does not contain glucose or sucrose, the extraction procedure is omitted, and the appropriate quantity of tablet basis is used to prepare the blank soln.

A. R. Rogers

2759. **Determination of chlorogenic acid [in tobacco].** A. S. Weaving (Res. Dept., Imperial Tobacco Co., Ltd., Raleigh Road, Bristol, England). *Nature*, 1957, **180**, 1287–1288.—Rutin and related polyphenols, which may be present in the solution as prepared for analysis, interfere with the method of Wilkinson *et al.* (*J. Ass. Off. Agric. Chem.*, 1954, **37**, 1004) for the determination of chlorogenic acid in flue-cured tobacco by oxidation with alkaline hypoiodite. A satisfactory method would require the quant. removal of polyphenols, probably by paper chromatography, along the lines suggested by Paech and Ruckenbrod (*Ber. dtsch. bot. Ges.*, 1953, **66**, 76).

R. E. Essery

2760. **The purity of chloroform B.P.** A. C. Caws and G. E. Foster (Wellcome Chemical Works, Dartford, Kent, England). *J. Pharm. Pharmacol.*, 1957, **9** (12), 824–833.—The "chloro compound" isolated during previous work on a source of error in the assay of strychnine salts and preparations (*cf. Anal. Abstr.*, 1957, **4**, 648) has been identified as strychnine chloromethobromide. It is formed by heating strychnine with bromochloromethane, which occurs to the extent of $\gtrsim 0{\cdot}5\%$ in all samples of chloroform B.P. examined. The presence of this impurity in chloroform has been confirmed by gas chromatography, which also revealed the presence of $\gtrsim 0{\cdot}1\%$ of dichloromethane as an additional impurity.

A. R. Rogers

2761. **Rapid chromatographic assay of acetylsalicylic acid, acetophenetidine [phenacetin] and caffeine.** J. Levine (Food and Drug Admin., Washington, D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (11), 687–689.—Double partition chromatography and spectrophotometry are used in this method for the assay of tablets of aspirin (**I**), phenacetin (**II**) and caffeine (**III**). A complete analysis requires < 1 hr. *Procedure*—Prepare a chromatographic column containing a mixture of Celite 545 (2 g) and 4 *N* H_2SO_4 covered by a layer of a mixture of Celite 545 (2 g) and *N* aq. $NaHCO_3$ (2 ml). Wash the column with diethyl ether (15 to 20 ml) and discard the washings. Prepare an extract of the powdered tablets (containing 50 mg of **I**) in $CHCl_3$ (50 ml) containing glacial acetic acid

(0·1 ml). Mix a 5-ml aliquot with diethyl ether (20 ml) and pour through the prepared column. To determine **II**, elute the column with diethyl ether (5 × 5 ml), collect the eluate and evaporate to dryness, dissolve the residue in $CHCl_3$ (5 ml), dilute to 50 ml with *iso*octane and measure the extinction at 285 mμ. Next, determine **III** by elution with $CHCl_3$ (50 ml) and measurement at 276 mμ. Finally, determine **I** and any salicylic acid formed by hydrolysis of **I** by elution with 1% acetic acid in $CHCl_3$ (100 ml) and measurement at 280 and 310 mμ. A. R. ROGERS

2762. **Determination of theophylline, pentobarbitone and papaverine in tablets by spectrophotometric analysis.** P. F. Helgren, F. E. Chadde and D. J. Campbell (Abbott Lab., North Chicago, Ill., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (11), 644–646.—This procedure is suitable for the analysis of tablets each containing theophylline (**I**) (76 mg), pentobarbitone sodium (**II**) (15 mg) and papaverine hydrochloride (**III**) (40 mg). The coeff. of variation of the results, determined from 10 replicates, is ± 0·65% for **I** and **III**, and ± 0·75% for **II**. *Procedure*—Shake the powdered sample (containing the equiv. of one tablet) for 2 min. with 1% aq. HCl (100 ml) and extract with diethyl ether (5 × 20 ml). Wash the combined ether extracts with slightly acid water (3 × 10 ml) and mix these water washings with the 1% HCl soln. Dilute the combined acid soln. to 200 ml with H_2O, then dilute a 2-ml aliquot to 100 ml with phosphate buffer (pH 6·2) and determine **I** and **III** by a 2-point spectrophotometric method based on the extinctions at 243·5 mμ and 272 mμ. Evaporate the washed ether extract without heat under N, dissolve the residue in 0·75 *N* aq. NH_3, filter if necessary, dilute a 5-ml aliquot to 50 ml with 0·75 *N* aq. NH_3 and determine **II** spectrophotometrically at 240 mμ. A. R. ROGERS

2763. **Titration of amidopyrine in non-aqueous solvents.** B. Láng and L. Tavaszy (Drug Supply Undertaking "Gyógyért", Budapest). *Z. anal. Chem.*, 1957, **158** (5), 339–347 (in English).—Dissolve the sample of amidopyrine (**I**) (200 to 250 mg) in benzene - glacial acetic acid (3 : 1) (20 ml) and titrate with 0·1 *N* $HClO_4$ in glacial acetic acid, with 1% diphenylamine orange in glacial acetic acid (2 drops) as indicator. The colour changes sharply from greenish yellow to pink at the end-point. The separation of a microcrystalline ppt. of **I** perchlorate starts at the end-point; with excess of $HClO_4$, the composition of the ppt. changes from **I**.$HClO_4$ to **I**.3$HClO_4$. The results of 11 determinations showed a mean recovery of 99·9% of **I** and a coeff. of variation of 0·17%. Smaller amounts of **I** (40 to 50 mg) may be titrated with 0·02 *N* $HClO_4$ with 99·7% recovery and a coeff. of variation of 0·33% (6 replicates). Salicylic acid, acetylsalicylic acid, barbiturates and moderate amounts of alkaloid hydrohalides do not interfere. A. R. ROGERS

2764. **Perchloric acid titration as a pharmacopoeia method.** I. Bayer and E. Posgay (Lab. Pharmakopöe-Kommission, Budapest). *Pharm. Zentralh.*, 1957, **96** (11), 561–567.—A method is suggested for the determination of pethidine, methadone, neostigmine and tolazoline by titration with 0·1 *N* $HClO_4$ which has been standardised with anhydrous K_2CO_3, with 0·1% gentian violet in acetic acid containing 3% mercuric acetate as indicator. A modification of the method is described for tolazoline in pharmaceutical preparations. D. P. FELIX

2765. **Spectrophotometric determination of Demerol [pethidine].** M. J. Pro and R. A. Nelson (Alcohol and Tobacco Tax Div. Lab., Internal Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1103–1108.—The narcotic sample is macerated with warm water, then centrifuged, and the soln. is distilled with steam after addition of a buffer soln. (pH 8). The distillate (250 ml) is acidified with HCl and the extinction is measured at 257 mμ against a 0·1 *N* HCl reference soln. For identification, the distillate is evaporated to dryness, the residue is extracted with ether in the presence of NaOH, and the dry ethereal extract is dissolved in CCl_4. The i.r. spectrum (1 to 15 μ) is compared with that (illustrated) of pethidine. A correction can be applied for the presence of phenacetin, which absorbs at the same wavelength. A. A. ELDRIDGE

2766. **Refractometric method for the quantitative determination of leptazol.** N. P. Yavorskiĭ (Lvov Med. Inst.). *Aptechnoe Delo*, 1957, **6** (5), 69–71.—Values of the refractive index at 20° are given for 5 to 20% w/v and v/v aq. soln. of leptazol. The results are applied to the refractometric determination of leptazol in pharmaceutical soln. E. HAYES

2767. **Voltammetry at solid electrodes. Anodic polarography of sulpha drugs.** J. D. Voorhies and R. N. Adams (Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 346–350.—Sulpha drugs show anodic waves with $E_{\frac{1}{2}}$ from + 0·75 to 1·05 V *vs.* the S.C.E. in the pH range 1 to 9 when studied by a current-scanning technique at a rotating platinum electrode. Sulphapyridine, sulphasomidine and sulphadiazine can be determined quant. in the range 4 × 10^{-5} to 1 × 10^{-4} *M* with a reproducibility of ≃ ± 2%. The determination of these drugs in blood and urine is not satisfactory because of large background currents. K. A. PROCTOR

2768. **Colorimetric determination of choline esters.** H. Benger and E. Kaiser (Hyg. Inst., Univ., Innsbruck). *Sci. Pharm.*, 1957, **25** (1), 1–7.—The method of Hestrin (*J. Biol. Chem.*, 1949, **180**, 249) for the determination of esters, based on the production of hydroxamic acids and their colour reaction with Fe^{3+}, has been modified by the use of hydroxylamine nitrate and ferric nitrate in HNO_3 soln. instead of hydroxylamine hydrochloride and $FeCl_3$ in HCl soln. The extinction is measured at 505 mμ. The procedure has been used for the determination of the acetate, succinate and adipate of choline and homologues. A. R. ROGERS

2769. **Methods for the determination of Tral [hexocyclium methylsulphate], a new anticholinergic drug.** P. F. Helgren, J. G. Theivagt and D. J. Campbell (Abbott Lab., North Chicago, Ill., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (11), 639–643.—Titration with 0·1 *N* $HClO_4$ in glacial acetic acid may be used to check the purity of hexocyclium methylsulphate (**I**) or to determine **I** in tablets not containing salts of weak acids. Procedures involving the combination of **I** with either (*A*) bromothymol blue or (*B*) ammonium cobaltothiocyanate to form a $CHCl_3$-sol. complex are suitable for the assay of tablets of **I**. Starch, Mg stearate, Na citrate and poly(vinylpyrrolidone) do not interfere with either procedure; polyethylene glycol 6000 interferes with procedure *A* but not with *B*. The coeff. of variation, determined from

10 replicates, is $\simeq \pm 1\%$. *Procedure A*—Mix an aq. extract of the tablets (5 ml, containing $\simeq$ 250 μg of **I**) with 0·15% bromothymol blue soln. (1 ml), borate buffer (pH 8·5) (15 ml) and $CHCl_3$ (25 ml) and shake mechanically for 10 min. Filter the lower layer through glass wool ($< 0{\cdot}1$ g), mix a 10-ml aliquot of the filtrate with 0·005 *N* methanolic NaOH (2 ml) and measure the extinction at 620 mμ against a $CHCl_3$ blank. *Procedure B*—Mix an aq. extract of the tablets (5 ml, containing $\simeq$ 1·5 mg of **I**) with 20 ml of a soln. of cobaltous nitrate (15 g) and NH_4SCN (100 g) in H_2O (500 ml). Shake for 1 min. and allow to stand for 5 min. Add $CHCl_3$ (5 ml) and shake vigorously for 1 min. Filter the lower layer through glass wool and measure the extinction at 620 mμ.

A. R. ROGERS

2770. **Determination of ethanol content of tinctures and spirits by means of the critical solution temperature.** R. Fischer and H. Auer (Pharmakognostische Inst. der Univ. Graz, Austria). *Pharm. Zentralh.*, 1957, **96** (10), 497–503.—The critical solution temperature method of Fischer and Resch (*cf. Anal. Abstr.*, 1955, **2**, 3183) has been applied to the determination of the ethanol content of tinctures and similar preparations. The sample must be shaken with activated carbon and filtered before the determination. Suitable reference liquids include ethyl phthalate (for ethanol contents in the range 58 to 70%) and 2:2-dichloroethyl ethyl ether (for 66 to 75% ethanol). Results by this method agree within $\pm$ 1% with those by distillation and determination of refractive index for 25 tinctures and spirits. Refractometric methods are described for the determination of menthol in spirit of peppermint and of camphor in spirit of camphor and in camphorated oil.

A. R. ROGERS

See also Abstracts—**2691**, Non-aqueous titration of phenolic compounds. **2725**, Determination of barbiturates in urine. **2825**, Use of cellulose ester paper in chromatography.

Food

2771. **Moisture determination by infra-red [technique] in food analysis.** F. Schierbaum (Inst. für Ernährungsforschung, Potsdam-Rehbrücke, Germany). *Dtsch. LebensmittRdsch.*, 1957, **53** (8), 173–178.—The experimental procedure and the apparatus are discussed. A 250 to 500-W lamp is used, the filament of which develops a temp. of 2000° to 2500° K; 1000° K is the most favourable temp. for drying animal and plant material. Data are presented on determinations of moisture in meat, fish and protein; in oils and fats; and in milk, starch and sugar products; comparison is made with results obtained by standard methods. The penetrating power of the rays is discussed and a sample thickness of 1 to 1·5 cm is suggested. The drying time is very considerably shortened by the i.r. method, *e.g.*, a result on a raw meat sample is obtained in 8 min. as compared with 1 hr. at 150° by the drying-oven method. I.r. methods give reproducible results which compare very favourably with those of standard methods. S.C.I. ABSTR.

2772. **Determination of tin in foods with the use of oscillographic polarography.** Z. Malkus (Hygiene Inst. Prague). *Z. LebensmittUntersuch.*, 1957, **106** (4), 257–262.—A rapid method for the determination of Sn in preserved fruits and vegetables by means of an Electrontube Polaroscope P-524 is described, and the oscillogram is illustrated for the prep. of the calibration curve $dV/dt = f(V)$. The concn. of Sn in HCl (10%) is shown by a sharp reversible indentation (the depolarisation effect of the Sn^{4+}), the depth of which is determined with the horizontal sliding axis of the calibrated shift which is simultaneously projected on the screen of the cathode-ray tube. The method is sensitive and is useful in routine determinations. Data on 20 kinds of material are given and results compare favourably with those obtained colorimetrically. Interference by $>$ 5 mg of Pb per 1000 g of test material can be neglected. S.C.I. ABSTR.

2773. **Determination of water in granulated sugar.** S. Hill and A. G. R. Dobbs (Tate and Lyle Res. Lab., Westerham Rd., Keston, Kent, England). *Analyst*, 1958, **83**, 143–149.—The sugar sample (15 g) is sealed in a thin glass ampoule which is then enclosed in a flask that can be evacuated. After evacuation of the flask the ampoule is broken, the sugar is finely ground by means of steel balls in the flask, which is mechanically shaken with a circular motion, and the water is driven from the sample by a thermostatically controlled heater and condensed in a second evacuated space of known vol. This space is then sealed and the condensed water is allowed to evaporate. The pressure of the vapour is measured manometrically and the amount of water present is thus ascertained. The apparatus is described in detail. Results show that the water in granulated sugar, usually $\simeq$ 0·04%, can be determined with a coeff. of variation of $< \pm 1\%$. Comparisons with other methods are made, and the distribution of water between the surface and interior of sugar crystals has been investigated.

A. O. JONES

2774. **A study of some methods for determining water in refined sugars, including the newly devised cobaltous bromide method.** S. D. Gardiner and H. J. Keyte (Tate and Lyle Res. Lab., Westerham Rd., Keston, Kent, England). *Analyst*, 1958, **83**, 150–155.—The apparatus used consists of a thick glass flask containing stainless-steel balls for grinding the sample by rotation of the flask, a filter-tube through which, by inversion of the assembly, the contents of the flask can be filtered into another flask, and "pipette" flasks by means of which reagents and solvents can be introduced into the sample flask under dry air conditions. To determine total water, the sugar sample (30 g) is ground with $CHCl_3$ and CCl_4 in the grinding flask for a period that ensures a final specific surface of 3500 $\pm$ 200 sq. cm per g. Standard cobaltous bromide soln. (150 mg per 20 ml in $CHCl_3$) is introduced into the flask and rotation is continued for 10 min. The liquid is then filtered into the second flask and the residual cobaltous bromide in an aliquot of the filtrate is determined by evaporation and weighing. The cobaltous bromide pptd. by reaction with the water in the sample is thus found and is referred to a calibration graph. Surface moisture is determined similarly, the grinding of the sample being omitted. Comparison is made with results of oven-drying and vacuum-distillation methods.

A. O. JONES

2775. **Colorimetric determination of saponin as found in beet sugars.** H. M. Bauserman and P. C. Hanzas (American Crystal Sugar Co. Res. Lab., Rocky Ford, Colo., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (10), 773–776.—In the extraction from

sugar (100-g samples) the saponin was pptd. with HCl, freed from fat with hot benzene and dissolved in hot methanol. This extract (5 ml) was made up to 10 ml with conc. H_2SO_4. The transmittance was measured at 575 mμ and again after addition of 1-naphthol (10% in methanol) (0·25 ml); 0 to 12 mg of saponin was found. The method was also tested by using 100-g portions of sugar, dissolving, acidifying, and filtering, and to the filtrates adding known amounts of saponin. Data indicate the efficiency of recovery. S.C.I. ABSTR.

2776. **Determination of bromine compounds in molasses from sugar factories.** A. R. Deschreider and J. Frateur. *Ind. Aliment. Agric.*, 1957, **74**, 541–544.—Direct determination of quaternary ammonium bromides by colorimetric determination of the bromophenol blue complex gave unsatisfactory results. A method for the colorimetric determination of total bromide, based on that of Pohl, was developed. This consisted in dry-ashing the molasses, after treatment with alkali, at 480° to 500°, followed by extraction, neutralisation, and the formation of tetrabromofluorescein. The natural bromine content of molasses was found to lie within the range 1·8 to 4·35 p.p.m., whereas samples suspected of containing quaternary ammonium compounds gave values of 7·5 to 50 p.p.m.
J. V. RUSSO

2777. **Relationship of the strength of high-solids pectin gels to the concentration and jelly-forming capacity of the pectin present.** P. Wade (Chivers and Sons, Ltd., Histon, Cambridge, England). *Nature*, 1957, **180**, 1067–1068.—Previous studies of pectin gels are reviewed. The linear relationship of log (gel strength) to log (pectin concn.) is shown to be represented by a general equation of the form $R = AP^n - B$, where R is gel strength, P is pectin concn., A and B are parameters, and n is $\simeq 2$.
D. G. FORBES

2778. **Colorimetric determination of α-amylase [in flour, malt and enzyme preparations].** G. Jongh (Centr. Inst. Voedingsonderzoek T.N.O.). *Chem. Weekbl.*, 1957, **53** (45), 597–602.—Some modifications of Hoskam's method are described. (*i*) A NaCl soln. is used for complete extraction; (*ii*) an excess of β-amylase is added since, in the absence of β-amylase, the result of the determination is 25% low; (*iii*) a logarithmic relation between activity and extinction is used as the basis of the determination.
P. RENTENAAR

2779. **Determination of the acidity of bread.** H. Rönnebeck. *Ernährungsforschung*, 1957, **2** (3), 527–539.—Procedures based on the titration of aq. extracts are criticised. In the method proposed, the sample (40 g) is continuously extracted for 3 hr. at 81° by 87% *iso*propyl alcohol (150 ml), and an aliquot portion of the extract is titrated with 0·1 *N* NaOH, with phenol red as indicator. This treatment yields $\simeq 4\%$ more titratable acid than is obtained by continuous extraction with acetone for 16 hr., and $\simeq 40\%$ more than the amount obtained by exhaustive intermittent extraction with *iso*propyl alcohol at room temp. After extraction with H_2O at room temp., the residues yield appreciable amounts of acid when further extracted with *iso*propyl alcohol. For the determination of volatile acids, a portion of the *iso*propyl alcohol extract (50 ml), mixed with anhyd. Na_2SO_4 (40 g), 2 *N* H_2SO_4 (10 ml) and 20% H_3PO_4 (10 ml), is steam-distilled for 35 min., and the distillate (200 ml) is titrated with 0·1 *N* NaOH, with phenol red as indicator.
P. S. ARUP

2780. **The determination of polyoxyethylene esters in bread and rolls.** R. A. Garrison, V. Harwood and R. A. Chapman (Food and Drug Directorate Lab., Ottawa, Canada). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1085–1093.—Polyoxyethylene 8 monostearate (added to bread to maintain "freshness") is extracted from dried bread by heating the ground sample with 6 *N* HCl for 10 min. at 100°, cooling, adding KOH and then K_2CO_3, and extracting the mass with $CHCl_3$. An aliquot of the centrifuged and filtered soln. is successively extracted with three portions of water, the extract then being treated at 100° with HCl, $BaCl_2$ soln. and molybdophosphoric acid soln. The washed ppt. is dissolved in H_2SO_4, diluted, and treated with NH_4SCN and $SnCl_2$. The extinction is read at 470 mμ against a reagent blank, and the result is read on a standard curve. For concn. normally employed, the results are accurate to about 5%.
A. A. ELDRIDGE

2781. **The rapid determination of moisture in meat products.** C. H. Perrin and P. A. Ferguson (Canada Packers Ltd., Toronto, Canada). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1093–1096.—The chopped sample (25 g) is oven-dried at 200° for about 15 min. The oven (2600 W), having a capacity of rather more than 1 cu. ft., has forced circulation, and the aluminium pan (8 in. × 8 in. × 2 in.) stands on a short-legged tripod. The accuracy and precision are good.
A. A. ELDRIDGE

2782. **Determination of calcium in milk and whey.** E. R. Ling (Nottingham Univ. School of Agric., Loughborough, England). *Analyst*, 1958, **83**, 179–182.—The milk or whey (5 ml) in a 100-ml flask is mixed with $\simeq$ 30 ml of water and then with 1 ml of dil. HNO_3 (1 + 2). After mixing, 10 ml of potassium metastannate soln. (prep. described) is added and the liquid is filtered. An aliquot (50 ml) of the clear or only slightly turbid filtrate is neutralised to pH test-paper with 0·5 *N* NaOH. A 2-ml portion of the NaOH soln. and 0·02 to 0·03 g of murexide indicator are added. The liquid is titrated from a burette, graduated in 0·02 ml, with aq. 0·4% EDTA (disodium salt) soln. until one drop changes the colour from pink to the violet colour of the standard (a saturated soln. of sodium tetraborate containing cresol red). The EDTA soln. is standardised against $CaCl_2$ soln. (2 g of $CaCO_3$ dissolved in the minimum amount of HCl and diluted to 1 litre). A blank determination, which is essential, is made exactly as described, with water in place of the sample. A method for correcting for the vol. of the ppt. is described.
A. O. JONES

2783. **An improved method for the determination of lactic acid in dried non-fat milk samples.** J. Velasco and C. R. Noll, jun. (Biol. Sci. Branch, Agric. Marketing Service, Beltsville, Md., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1081–1084.—The sample is deproteinised by treating it with 80% aq. methanol, shaking (15 min.), cooling at 5° to 10° (1 hr.) and filtering. The extract is then passed through cation- and anion-exchange resins, and eluted as lactate from the latter resin with *N* Na_2CO_3. Colour is developed by addition of *p*-phenylphenol and read at 570 mμ, the lactic acid concn. being read from a standard curve. The purification procedure removes carbohydrates

amino acids and acetaldehyde. Lactic acid added to a dried milk sample was completely recovered.
A. A. ELDRIDGE

2784. **Determination of alkali metals in milk by flame photometry.** F. Jurčík and F. Šebela (High School of Agric., Brno, Czechoslovakia). *Průmysl Potravin*, 1957, **8** (3), 153.—The usual flame-photometric determination of Na and K has been found suitable for the analysis of milk. A new procedure for the decomposition is suggested. *Procedure*—Evaporate the sample (10 ml) to dryness with acetic acid (0·5 ml) in a platinum dish at 110° to 120°, ignite the residue, wash with hot water and filter. Repeat the procedure with the filtrate and ignite at 500°. Dissolve the residue in HCl (10%) (10 ml), filter, dilute to 100 ml and carry out the flame-photometric determination. The amount of Ca in milk has no influence on the determination.
J. ZÝKA

2785. **Identification and determination of strontium-90, especially in milk.** A. Miserez (Service Fédéral de l'Hygiène Publique, Berne). *Mitt. Lebensmitt. Hyg., Bern*, 1957, **48** (6), 468–476 (in French).—Of the principal components of radio-active fall-out from nuclear bomb tests, ^{90}Sr is the most dangerous because it becomes concentrated in milk and in the bones of infants, where it causes irreversible damage. The concn. of ^{90}Sr in milk can be determined by three methods. (*i*) The total activity of an ashed sample is measured, total K is determined and a correction made for the activity due to the naturally occurring ^{40}K. (*ii*) The insoluble oxalates are pptd. from a soln. of the ash and their activity is measured. (*iii*) The concn. of ^{90}Y, which is in equilibrium with ^{90}Sr, is determined after pptn. with boiling aq. NH_3 in the presence of inactive Y and Sr as carrier and hold-back carrier, respectively. The rate of decay identifies ^{90}Y and hence the parent ^{90}Sr. Results obtained by the three methods are in agreement, the third method being the most sensitive.
G. BURGER

2786. **Determination of phosphatase in milk.** Torakichi Yoshioka and Isamu Tani (Tokushima Univ.). *Eisei Kagaku*, 1957, **4**, 89–91.—Phenolphthalein is liberated from Na phenolphthalein diphosphate by the action of phosphatase in milk in weak alkaline medium, and the extinction of the coloured soln. at 550 mμ is measured.
CHEM. ABSTR.

2787. **Detection of adulteration of animal fat in ghee by critical temperature of dissolution.** O. Prakash, A. C. Gupta, V. D. Athawale and S. Rai (H.B. Technol. Inst., Kanpur, India). *J. Oil Technol. Ass., India*, 1956, **12** (2), 131–134.—The critical temp. of dissolution (C.T.D.) is used for the detection of 10% of adulterant in ghee. *Procedure*—Free fatty acids are removed by dissolving 15 g of sample in 25 ml of ethanol (95%) and keeping at 60° for 10 to 15 min. when the fatty layer is removed and similarly extracted with ethanol, the alcohol being finally removed. A 2-ml portion of this molten material is mixed with 2 ml of ethanol-*iso*amyl alcohol (2:1) and heated until a clear soln. is obtained. Then on cooling slowly, the temp. at which a turbidity occurs is taken as the C.T.D. Values of C.T.D. for pure ghee range from 49·5 to 53·5, and are > 73 for tallow.
G. R. WHALLEY

2788. **Polarographic determination of oxygen in fruit juices.** A. Monzini and G. Botalla (Sta. Expérimentale du Froid, Milan). *Chim. Anal.*, 1957, **39** (10), 383–384.—The apparatus used includes a polarograph that gives 100 mm deviation per 0·105 mA, and a cell, not described, that enables the sample to be introduced and analysed out of contact with air. Readings were taken at 0·4 V at temperatures between 28° and 34°, under which conditions it is claimed that significant differences in diffusion current between juices were not observed. Very small concn. of O, $\simeq$ 0·02%, could be measured with a percentage error $\gtrsim \pm$ 2%. Samples of juices from the Italian market generally had O contents < 0·02%, and fresh juices gave figures from 0·25% to 0·80%, the differences being ascribed to ageing. It is noted that de-aerated juices take up O markedly when bottled by gravity, but not when bottled under vacuum. The importance is stressed of de-aeration before application of heat, and the prevention of re-aeration in the filling machine.
R. E. ESSERY

2789. **Optical polarisation detection of apple pulp in preparations of various fruits.** A. T. Czaja (Botanischen Inst. der Tech. Hochschule, Aachen, Germany). *Z. LebensmittUntersuch.*, 1957, **106** (4), 262–271.—The parenchyma cells of apple mesocarp (pulp) have thicker cell walls than have those of most other fruit pulp cells used commercially. The walls of such radial cells show statistical optical isotropy when viewed directly (perpendicularly). The long axes of the index ellipsoids lie tangentially in the surface of the walls, so that in longitudinal section doubled-back margins and folds of the cell walls and other deep folds in parallel to the cellulose micelle result, and these areas are anisotropic and double refracting ("Folienstruktur"). When examined microscopically in single cell layers between crossed Nicol prisms with sensitive gypsum compensators red I, brighter and "higher" interference colours of these areas are observed. The detection by this method of apple pulp when mixed with each of 20 varieties of other fruit pulps is discussed.
S.C.I. ABSTR.

2790. **Determination of added distinctive cations in whisky. X. Spectrophotometric determination of zinc.** R. A. Nelson and M. J. Pro (Alcohol and Tobacco Tax Div. Lab., Internal Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1100–1103.—The sample of whisky (5 ml) is shaken with $Na_2S_2O_3$ soln. (25% w/v) (2 ml) and an acetate buffer soln. (pH 4·5) (15 ml), followed by dithizone soln. (0·001% in CCl_4) (10 ml). The Zn in the CCl_4 and the reagent blanks is determined spectrophotometrically at 540 mμ. By this method 1 p.p.m. of Zn can be determined in the presence of many other cations to within 0·15 p.p.m.
A. A. ELDRIDGE

2791. **Determination of moisture in hops.** G. J. Haas and A. I. Fleischman (Liebmann Breweries, Inc., Brooklyn, N.Y., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (10), 776–779.—Comparative data on the various methods for the determination of moisture in hops, with special emphasis on the use of the Karl Fischer reagent, are presented. Lower moisture values were obtained by Karl Fischer titration and by solvent distillation with *iso*octane than by oven-drying or solvent distillation with toluene or benzene. The Karl Fischer method appears to be more accurate than the last three mentioned methods.
S.C.I. ABSTR.

2792. **A paper-chromatographic procedure for the separation and identification of coumarin, dihydrocoumarin (melilotin) and 6-methylcoumarin.** L. C. Mitchell (Div. Food, Food and Drug Admin.,

Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1029–1033.—The procedure described is for application to these compounds after their separation from food materials in essentially pure condition. The immobile solvent comprises dimethylcyanamide (4 ml), formamide (2 ml) and ethanol (25 ml) in diethyl ether (to 100 ml); the mobile solvent is light petroleum. The chromogenic agent is KOH (11 g in methanol to 200 ml). R_F values are given. A. A. ELDRIDGE

2793. **Partition chromatography on filter-paper of the synthetic colours authorised for use in food.** R. C. T. Puche. *Rev. Asoc. Bioquim. Argentina*, 1957, **22**, 228–236.—A two-dimensional chromatogram is obtained with *n*-butanol satd. with 10% HCl and xylidine in dil. HCl (1:2) as solvents. R_F values are given for the colours in both solvents. Some colours are discharged by the xylidine-HCl reagent and are regenerated by exposing them to NH_3. Final identification is by dyeing wool with the sample and observing the action of the following reagents—conc. H_2SO_4, 10% H_2SO_4, conc. HCl, conc. HNO_3, 10% NaOH soln., and 10% $SnCl_2$ soln. in HCl. G. H. FOXLEY

2794. **Chromatographic detection of sorbic acid used as a preservative in beverages.** E. Sudario (Oenolog. Expt. Sta., Asti, Italy). *Chim. e Ind.*, 1957, **39** (10), 811–814.—The use of sorbic acid (**I**) as an antifermentative in sweet wines, and methods of detection, are reviewed. **I** may be identified by the steam-distillation of a sample of wine in the presence of syrupy H_3PO_4, extraction of the distillate with diethyl ether, evaporation of the ether, dissolution of the residue in dil. aq. NH_3 and chromatography. *n*-Butanol satd. with 1·5 *N* aq. NH_3 is used as the mobile phase, with 1·5 *N* aq. NH_3 satd. with *n*-butanol as the stationary phase. **I** is identified by the formation of a grey colour when the paper is sprayed with 0·5% ethanolic bromocresol purple. The R_F value is 0·53.
A. G. COOPER

2795. **Identification of edible oils and the detection of oil adulteration by differential infra-red spectroscopy.** J. C. Bartlet (Dept. of Nat. Health and Welfare, Ottawa, Canada). *Nature*, 1957, **180**, 1071–1072.—Under examination with a Perkin-Elmer Model 21 double-beam i.r. spectrophotometer, in sodium chloride cells of 1-mm path length and with a speed of 100 cm^{-1} per min., 10% soln. of oils and fats in CCl_4 give characteristic absorption spectra in the frequency range 1200 to 900 cm^{-1}. The slit is adjusted to a width of 300 μ. If a sample soln. is compared against a soln. of the pure oil, variations in the differential spectra can be interpreted to detect adulterations, or for rapid characterisation. Estimates of the proportion of extraneous oils in a given sample also compare favourably with results obtained by classical methods. D. G. FORBES

2796. **Determination of rancidity of oils and fats.** T. L. Pepe and A. Vestita (Via R. Elena 107, Taranto, Italy). *Olii Min.*, 1957, **34** (11), 480–481.—Deficiencies in existing tests are discussed and a new procedure is proposed. The oil or fat (30 g) is heated on a water bath in a special type of extractor with 0·1 *N* NaOH (2 ml) and H_2O (100 ml). When 20 ml of distillate has been collected it is cooled and shaken with HCl (10 ml) followed by 0·1% phloroglucinol in ether (5 ml). Rancidity is denoted by a pink or red colour in the acid layer.
L. A. O'NEILL

2797. **Significance of refractive index of refined olive oils.** T. N. Plebani and G. Bigoni (Gaslini S.A., Genoa). *Olii Min.*, 1957, **34** (10), 451–452.—The refractometer readings of genuine expressed olive oils are normally within the official limits of 61 to 63, but tests on a large number of genuine refined olive oils from several seasons showed normal limits for these oils to be from 63 to 66. Refined oils of refractometer reading less than 63 require more detailed examination before acceptance as genuine. E. C. APLING

2798. **Fitelson's test for tea-seed oil in olive oil.** G. Bigoni (Gaslini S.A., Genoa). *Olii Min.*, 1957, **34** (10), 458.—Many genuine olive oils give a slight pink colour in Fitelson's test, in some cases approaching the colour given by 10% of tea-seed oil (*cf.* AOCS Official Method Cb 3–39). It is concluded that a positive Fitelson reaction is completely reliable only when more than 15% of tea-seed oil is indicated. E. C. APLING

2799. **Chromatographic separation of five vitamin-A_1 isomers from the eyes of deep-water prawns (*Pandalus borealis*).** B. Barnholdt and W. Hjarde (Statens Vitamin-Lab., Copenhagen, Denmark). *Acta Physiol. Scand.*, 1957, **41** (1), 49–67 (in English).—The unsaponifiable matter is dissolved in light petroleum and chromatographed on alumina (17 cm × 1·8 cm column), eluting with an ether - light petroleum mixture (20 to 60% v/v of ether). The isolated vitamin A is dissolved in light petroleum and is chromatographed on di-calcium phosphate (78 cm × 3·0 cm column). Elution is carried out with light petroleum containing 3 to 7% v/v of ether, the eluate is collected in 5-ml fractions, and the ratio E_{310} to E_{325} is measured directly on the fractions. Five peaks were identified as corresponding to 11:13-di-*cis*, 11-mono-*cis*, 13-mono-*cis*, 9:13-di-*cis* (uncertain), and all-*trans* vitamin A_1, the ratio being 1·5:49:17:1·5:31. H. F. W. KIRKPATRICK

2800. **Determination of total ascorbic acid by the use of a suspension of *Erwinia solanisapra*.** I. E. Gero, P. Le Gallic and A. Bourdeau (Lab. de Physiol., 16, rue de l'Estrapade, Paris). *Bull. Soc. Chim. Biol.*, 1957, **39** (11), 1257–1269.—The sample soln. (*e.g.*, a 20% HPO_3 extract of tissue) is adjusted to pH 6·2 with a saturated soln. of K_2HPO_4, and to 3 ml are added 2 ml of bacterial suspension and 1 ml of freshly prepared 20% glucose soln. After 10 to 15 min. incubation at 37°, 1 ml of 20% HPO_3 soln. is added and the liquid is titrated with 2:6-dichlorophenolindophenol. The sample soln. is also titrated directly with the dye, and the difference in the two results gives the dehydroascorbic acid present.
H. F. W. KIRKPATRICK

See also Abstracts—**2752**, Determination of amylolytic activity. **2818**, Determination of spray residues in foods. **2820**, Determination of diazinon in milk.

Sanitation

2801. **Continuous sampling and ultra-micro determination of nitrogen dioxide in air.** M. B. Jacobs and S. Hochheiser (Dept. Air Pollution Control, New York, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 426–428.—From 0·4 to 4 p.p.m. of NO_2 in urban atmospheres can be determined continuously

by aspirating air (≃ 1·3 litres per min.) through a fritted-glass bubbler containing 30 to 35 ml of 0·1 *N* NaOH and 0·2% (v/v) of butyl alcohol. Twenty-four 40-min. samples are thus obtained, and the NO_2 in each is determined, after oxidising SO_2 with 1% H_2O_2 (1 drop), by diazotisation of sulphanilamide in 5% (v/v) H_3PO_4 followed by coupling of the diazo compound with 0·1% aq. N-1-naphthylethylenediamine dihydrochloride. After ≃ 30 min. the extinction of the soln. (50 ml) is measured at 550 mμ in matched cells (40 mm × 20 mm) against the reagent blank. W. J. BAKER

2802. **Determination of dimethylaniline in the air of industrial premises.** L. A. Zil'berg. *Gigiena i Sanit.*, 1957, (6), 83–84; *Ref. Zhur., Khim.*, 1957, Abstr. No. 74,717.—The method is based on the formation of an azo dye by the reaction of dimethylaniline (**I**) with sulphanilic acid (**II**) and HNO_2. Draw 25 litres of the air at a rate of 25 litres per hr. through 3 small absorbers, each containing 2 ml of 0·01 *N* H_2SO_4. Transfer 1 ml of the liquid in the tubes into 3 separate colorimetric tubes. At the same time prepare standards containing 0 to 0·0008 mg of **I**. To each sample and standard tube add 1 ml of reagent soln. [0·2 g of **II** dissolved in 20 ml of 0·1 *N* NaOH, and 20 ml of $NaNO_2$ (1 mg per ml), made up to 100 ml; prepared immediately before use], mix, set aside for 45 min., add 2 drops of *N* HCl and measure the extinction. The sensitivity of the method is 0·02 mg of **I** in 2 ml of soln. C. D. KOPKIN

2803. **The spectrographic determination of trace metals in natural waters.** Z. Nagy and E. N. Pólyik (Med. Univ., Debrecen, Hungary). *Magyar Kém. Foly.*, 1957, **63** (11), 297–302.—A logarithmic rotating sector is used in the method described for the detection and semi-quant. determination of the most usual trace metals in the dry residue of natural waters. The excitation is carried out by means of an arc, Be or Au is used as reference element, and the results are evaluated from the difference in the lengths of the lines given in the paper, and an experimentally obtained curve. The lowest concn. that can be determined (calculated as dry residue) is 0·0005 to 0·001%. This method cannot be used if the dry residue exceeds 500 to 800 mg and if the alkali content is more than 10 to 20%. In another method, a preliminary enrichment is carried out by means of dithizone or 8-hydroxyquinoline. The determination is similar to that described above, but the lengths of the lines are measured and the evaluation is carried out by means of a calibration curve. High salt concn. do not interfere, and 0·8 to 100 μg of metal per litre can be determined. A. G. PETO

2804. **Volumetric determination of sulphate in waters.** R. Geyer and K. Doerffel (Inst. für anal. Chem., Tech. Hochschule für Chemie, Leuna-Merseburg). *Z. anal. Chem.*, 1957, **158** (6), 418–421.—Filter the sample (containing 50 to 500 p.p.m. of SO_4^{2-}) and pass the filtrate through a column of a cation-exchange resin (Na form). Evaporate 100 ml of the eluate to 25 ml, add methanol (25 ml) and 25% acetic acid (2 ml) and titrate with 0·05 *N* $BaCl_2$, with a 0·1% aq. soln. of Na alizarinsulphonate (0·2 ml) as adsorption indicator (*cf.* Geyer, *Anal. Abstr.*, 1955, **2**, 3037). The standard deviation is estimated from 8 replicates to be ≃ ± 4 p.p.m. of SO_4^{2-}. A. R. ROGERS

2805. **Applications of a colorimetric micro-determination of phosphorus to waters treated with polymetaphosphates.** G. Van Beneden (Cébédeau, Liége, Belgium). *Bull. Centre Belge Étude et Document. Eaux*, 1957, (35), 33–40.—The soln., containing 0·01 to 0·06 mg of P in 10 ml of 2% H_2SO_4, is treated with 2 ml of 5% ammonium molybdate soln. After 5 min., 1 ml of 20% Na_2SO_3 soln. is added, followed by 1 ml of 0·5% quinol soln. The mixture is shaken, then allowed to stand for 25 min., and the percentage transmission read in a 14-mm cuvette at 650 mμ, against a reagent blank. Results are referred to a standard curve on semi-log paper, prepared by the use of Na_2HPO_4. Metaphosphates give a less intense colour with this procedure, and must be hydrolysed to orthophosphate by boiling 50 ml of the acid soln., mentioned above, under reflux for 30 min., diluting to volume if necessary, and treating 10 ml as before. When ortho- and polymetaphosphates are present together, a series of known soln. of orthophosphate is prepared, each being divided into a sub-series with increasing known doses of polymetaphosphate. These are examined before and after hydrolysis, the results enabling the degree of interference of the polymetaphosphate with the orthophosphate colour to be established. The unknown, after suitable defecation to remove organic phosphorus compounds, is similarly treated and compared with the standards. In the analysis of treated waters, the sample is brought to 2% acidity with conc. H_2SO_4, hydrolysed and treated as before. Some samples may require concentration by evaporation to bring the P into the required range. Under the conditions given, amounts of SiO_2 normally present in natural waters do not interfere but, when silicate is used for treatment, the blank and standard curve should be prepared by using the same water with the silicate but without the polymetaphosphate. In ferruginous waters, Fe is reduced and does not interfere in amounts 10 times that of the polymetaphosphate, but the latter interferes with the determination of Fe by the thiocyanate method, but not with the dipyridyl method. R. E. ESSERY

2806. **The determination of monobromoamine and monochloroamine in water.** J. K. Johannesson (Wellington City Council Lab., Wellington, New Zealand). *Analyst*, 1958, **83**, 155–159.—Methods for differentiating between monobromoamine and monochloroamine in chlorinated water containing both bromide and NH_3 (*e.g.*, sea-water swimming pools) are surveyed, and two methods are found to be suitable. The neutral *o*-tolidine and sodium hexametaphosphate reagent of Palin (*J. Inst. Wat. Eng.*, 1947, **3**, 100) forms with free Cl, free Br and NH_2Br, but not with NH_2Cl, a blue compound that can be measured either colorimetrically or by titration with $FeSO_4(NH_4)_2SO_4$ soln. This method does not distinguish between free Cl, free Br and NH_2Br, but Cl does not react after addition of an excess of an ammonium salt. It is not applicable to sea water owing to pptn. of magnesium salts by the phosphate buffer. In the second method, the test sample (200 ml) is placed in an amperometric titration apparatus set at zero applied volts, $NaHCO_3$ (0·2 g) is added, the current reading is noted and *N* $(NH_4)_2SO_4$ (1 ml) is added. A large reduction of current indicates the presence of free Cl or Br; no reduction indicates the presence of the combined forms. The soln. is now titrated with a phenyl arsenoxide soln. (standardised against iodine) until no further change of current occurs. A 1% soln. of KI (1 ml) is now added and titration

is continued, the additional titre representing either Cl or NH_2Cl. Results by the two methods agree satisfactorily. A. O. JONES

2807. **Treatment of water for marine boilers.** British Standards Institution (2 Park St., London). B.S. 1170:1957, 75 pp.—Three basic methods of chemical treatment are described for water for marine boilers with working pressures up to 850 lb per sq. in., and methods of testing for alkalinity, chlorides, hardness, phosphate, sulphites, sulphates, nitrate, dissolved solids and dissolved oxygen are appended. O. M. WHITTON

2808. **Separation and differentiation of mixtures of 2:3-4:5-bis(Δ^2-butenylene)tetrahydrofurfural [fly-repellent R-11], its alcohol and its acid by paper chromatography.** L. C. Mitchell (Div. of Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (10), 748–749.—Details are given of the ascending chromatographic procedure. The sensitivity is best ($\simeq$ 1 μg) 5 min. after the mobile solvent starts to ascend the paper, but separation is poorest. Separation is best after 1 hr., but sensitivity is poorest, *i.e.*, for the aldehyde, 3 to 4 μg; for the alcohol, 2 to 3 μg; and for the acid, 1 to 2 μg. Average R_F values are given. S.C.I. ABSTR.

2809. **Determination of small quantities of 2:3-4:5-bis(Δ^2-butenylene)tetrahydrofurfural (repellent R-11) in milk.** P. E. Toren, D. L. Goodhue, W. R. Kirkham and D. E. Howell (Res. Div., Phillips Petroleum Co., Bartlesville, Okla.). *J. Agric. Food Chem.*, 1957, **5** (10), 749–753.—This repellent was administered as a spray to Holstein cows in barns, daily, for five weeks at a level 10 to 20 times that needed for effective fly control. Milk samples were analysed by separating the butterfat from the milk, extracting the purified fat with *iso*octane and methanol and treating the extract with 2:4-dinitrophenylhydrazine. Portions of the *iso*octane phase were examined spectrophotometrically at 338 mμ. The partition coeff. of R-11 between butterfat and water was measured and the fraction of a known amount of R-11 added to a sample of milk was recovered in the separated fat. R-11 was not found in the milk samples from the treated cows although the method is sensitive to 0·1 p.p.m. S.C.I. ABSTR.

2810. **Separation and identification of antu [α-naphthylthiourea], Pival [pindone, 2-pivaloylindane-1:3-dione], and warfarin [3-α-acetonylbenzyl-4-hydroxycoumarin] by paper chromatography.** L. C. Mitchell (Div. Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1034–1037.—In the procedure described, the immobile solvent is dimethylacetamide (4% v/v) in diethyl ether, and the mobile solvent consists of mixed octanes, the chromatogram being viewed in u.v. light. The colours, in ascending order, are—warfarin, purple; antu, bright blue; pindone, buff. Antu affords additional spots when the chromatogram is lightly sprayed with KOH (11 g in methanol to 200 ml) and then viewed in u.v. light. R_F values are recorded. A. A. ELDRIDGE

See also Abstracts—**2571**, Determination of Pb in water. **2614**, **2615**, Determination of U in water. **2632**, Determination of Fe and Al in water.

Agriculture and Plant Biochemistry

2811. **Flame-photometric determination of manganese, iron and copper in plant material.** A. D. Berneking and W. G. Schrenk (Kansas Agric. Expt. Sta., Manhattan, U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (10), 742–744.—The plant material (2 g) is ashed at 500° for 16 hr., the residue is dissolved in HCl, 8-hydroxyquinoline soln. (5%) (10 ml) and $AlCl_3$ soln. (as a carrier pptg. agent) are added and the pH is adjusted to 5·1. The ppt. obtained, containing Cu and Fe, is ignited at 850° for 16 hr., finally dissolved in 0·1 *N* HCl (5 ml) and analysed in a Beckman Model DU flame spectrophotometer with photomultiplier attachment. The emissions for Cu and Fe are measured at 324·8 and 372 mμ, respectively. 8-Hydroxyquinoline soln. (5 ml) is added to the filtrate from the pptn. of Cu and Fe, the pH is adjusted to 7·1, and the resulting ppt. is treated as described for Cu and Fe. The final soln. is examined for Mn at 403·3 mμ. Results compared well with those of AOAC methods. S.C.I. ABSTR.

2812. **Colorimetric determination of ammonia in soil by means of the thymol - hypobromite reaction.** L. N. Lapin, R. Kh. Zamanov and V. P. Makarova. *Pochvovedenie*, 1957, (4), 95–98; *Ref. Zhur., Khim.*, 1957, Abstr. No. 77,374.—A method is described for the direct determination of NH_3 in soil without the preliminary preparation of an aqueous salt extract. Place the sample (100 to 800 mg) of air-dry finely ground soil in a 50-ml flask, add 5 ml of water, shake, add 0·8 ml of thymol soln. (6·25 g of thymol in 25 ml of ether), mix, add dropwise 10 ml of NaBrO soln. (to 300 ml of cold water add 3 ml of pure Br, shake vigorously, cool to 3° and pour into 150 ml of NaOH soln. of sp. gr. 1·32), with continuous shaking, and keep for 30 min. with shaking every 2 or 3 min. Extract the colour with 5 ml of a mixture of amyl alcohol and toluene (1:3). To 2 ml of the coloured upper layer in a 5- or 10-ml cylinder add an equal volume of amyl alcohol, mix and measure the extinction of the soln. Compare with suitable standards. The results vary by $\pm$ 1 mg of NH_3 for 100 g of soil. The method may be used under field conditions. C. D. KOPKIN

2813. **Rapid colorimetric estimation of soil phosphorus using a stable dry-powder reductant.** S. N. Edson (Univ. of Florida, Gainesville, U.S.A.). *Chemist Analyst*, 1957, **46** (4), 105, 112.—The reduction of the molybdophosphate ion to the blue complex is effected by the addition of a powder containing sodium sulphite (11 g), sodium hydrogen sulphite (277 g) and *p*-methylaminophenol sulphate (0·4 g). The powder is stable for indefinitely long periods. G. S. ROBERTS

2814. **Determination of potassium in compound fertilisers by flame photometry.** P. H. Martens (Inst. Agronom. de l'État, Lab. de Chim. Anal., Gembloux, Belgium). *Chim. Anal.*, 1957, **39** (10), 361–365.—Errors due to substances likely to be found in fertilisers are discussed. It is shown that although NaCl, $MgCl_2$, NH_4Cl and $(NH_4)_2SO_4$ have little effect, $CaCl_2$ leads to high results and $(NH_4)_2HPO_4$ to low ones, at ratios of K_2O to CaO and K_2O to P_2O_5 of 1:1. From experiments with synthetic mixtures a series of triangular diagrams is derived from which, given the proportions of CaO and P_2O_5 and the apparent K_2O from the photometer calibration curve, the correction to be applied to the photometer reading may be derived

Results for 50 fertilisers, checked by the chloroplatinate method, showed a relative error of ± 6·5% and a relative precision of ± 2·78%. In the analysis of clays, the interfering ions are usually removed before photometry, and the unknown obtained by reference to two standards, one on either side of the unknown. The present method is not suitable for use in cases of dispute, but can be employed for screening and control purposes.

R. E. ESSERY

2815. **A colorimetric procedure for phosphorus in feeds and marine products.** B. Gersten (Mass. Agric. Exp. Sta., Amherst, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1056–1059.—The sample (2 g) is digested with HNO_3 (30 ml) and H_2SO_4 (10 ml) and the resulting soln. is diluted to 200 ml. Aliquots are treated with $HClO_4$ (2·5 ml) and a soln. (0·8 ml) of 1-amino-2-naphthol-4-sulphonic acid (0·125 g) in 15% $NaHSO_3$ soln. (44 ml). After 0·5 min., 2 ml of 5% ammonium molybdate soln. is added, and the mixture is diluted to 25 ml. The extinction is read spectrophotometrically at 730 mμ, and the results are read from a standard curve. The method is rapid and sufficiently accurate for control work.

A. A. ELDRIDGE

2816. **Determination of free and total gossypol in mixed feeds containing cottonseed meals.** W. A. Pons, jun., and C. L. Hoffpauir (S. Regional Res. Lab., Agric. Res. Service, New Orleans, La., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1068–1080.—In the procedures described, free gossypol is extracted with a mixture of *iso*propyl alcohol, hexane and water containing a gossypol-complexing agent (3-aminopropan-1-ol) which prevents interference by feed constituents and stabilises gossypol during extraction. Total gossypol is extracted by means of a solution of 3-aminopropan-1-ol in dimethylformamide. The complexed gossypol is caused to react with aniline, and the dianilinogossypol is determined spectrophotometrically at 440 mμ against standards. Recoveries of 76·9 to 95·9% of free gossypol and of 96·5 to 106·5% of total gossypol are reported. The free gossypol content of mixed feeds falls appreciably on storage at room temperature, mainly owing to binding with feed constituents.

A. A. ELDRIDGE

2817. **Chemical determination of piperazine [present] as the dihydrochloride in feeds and concentrates.** M. L. Leng (Dow Chem. Co., Midland, Mich., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1059–1068.—In the procedure described, the piperazine is extracted from the feed by means of 0·1 *N* NaOH in ethanol. The diluted extract is filtered and acidified with HCl, and is then passed through a Dowex-resin chromatographic column, which is afterwards eluted with *N* NaOH. The eluates are neutralised (phenolphthalein) and treated with picric acid (10%) in ethanol. The pptd. piperazine dipicrate is collected, washed with ethanol and diethyl ether, dried for 1 to 2 hr. in a vacuum-desiccator and weighed. Recoveries of 83·2 to 107% of piperazine added to various feeds are reported.

A. A. ELDRIDGE

2818. **Detection and determination of spray residues in relation to food inspection.** J. Eichenberger (Städt. Lab., Zurich). *Mitt. Lebensmitt. Hyg., Bern*, 1957, **48** (6), 396–412.—Biological methods in conjunction with paper chromatography are preferred to chemical methods. Four procedures are described.

G. BURGER

2819. **Polarographic determination of dimethyl 2:2:2-trichloro-1-hydroxyethylphosphonate (Bayer L 13/59) [Dipterex].** P. A. Giang and R. L. Caswell (Entomology Res. Branch and Plant Pest Control Branch, U.S. Dept. of Agric., Beltsville, Md., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (10), 753–754.—A polarographic procedure was developed for the analysis of technical grades. The measurements were made with the Sargent pen-recording Model XXI polarograph. An H-cell with a S.C.E. in the anode compartment was used, suspended in a water bath maintained at 25° ± 0·5°, and the test soln. contained an aliquot of Bayer L 13/59 (1 g in 500 ml of water), 0·02 *N* KCl as the supporting electrolyte and 0·002% of gelatin as the max. suppressor. An accuracy of ± 2% is attained under the specified conditions, and the $E_{\frac{1}{2}}$ *vs.* the S.C.E. = − 0·68 V.

S.C.I. ABSTR.

2820. **Radioactive synthesis, detection and chromatography of an organic phosphorus insecticide: diethyl 6-methyl-2-*iso*propyl-4-pyrimidinyl phosphorothionate [diazinon]. Application to its determination in milk.** J. P. Vigne, R. L. Tabau, J. Chouteau and J. Fondarai (Lab. des Isotopes, Centre de Lutte contre le Cancer, Marseille, France). UNESCO/NS/RIC/99, 1957, 16 pp. (in French).—The synthesis of diazinon (**I**) containing ^{32}P is described. The chromatographic separation of **I** from common impurities was achieved by development with aq. NH_3 (sp. gr. 0·921) - ethanol - H_2O (1:3:5) on Whatman No. 1 filter-paper impregnated with silicone grease. The behaviour of **I** was studied by measuring the activity due to ^{32}P in the excreta and milk of a goat which had been fed with **I**.

G. J. HUNTER

2821. **Determination of dithiocarbamate fungicide residues.** H. L. Pease (Grasselli Chem. Dept., Du Pont de Nemours & Co. Exp. Sta., Wilmington, Del., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 1113–1118.—In the CS_2 evolution method for the determination of dithiocarbamate residues, a reaction flask of minimum size is used, all junctions are of glass, the contact surface in the Viles' reagent absorption tower is increased by lengthening the column, and the quantity of sample is limited to a maximum evolution of 100 μg of CS_2. The procedure is described. Recoveries of 89 to 102% of added dithiocarbamates are reported. By means of a stripping procedure in which EDTA (disodium salt) is used, at least 90% recoveries of zinc and manganese ethylene-1:2-bisdithiocarbamates (zineb and maneb) can be achieved.

A. A. ELDRIDGE

See also Abstracts—**2611**, Determination of Mo. **2823**, Separation of DDT by chromatography.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2822. **Separation in series of mixtures by liquid chromatography on columns.** H. Schlierf (Farbwerke Hoechst A.-G., Frankfurt a. M.). *Z. anal. Chem.*, 1957, **159** (2), 118–123.—Multiple chromatographic separations are carried out by running in parallel several column-chromatography units. The course of the separation is recorded on cotton yarn,

impregnated with suitable reagents, which is drawn through the eluate as it emerges from the column and wound on to a drum. In order that the chromatograms may be compared, the rates of flow must be the same for all the columns. This is effected by a special arrangement for the supply of solvent (illustrated). The separation of phenol, cresol and xylenols is given as an example.

J. H. WATON

2823. **Ascending paper chromatography.** L. C. Mitchell (Div. Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (4), 999–1029.—The techniques of paper chromatography are described, and examples of the application of the method are given. Whereas the aqueous solvent system shows only one spot for technical DDT, the non-aqueous system separates the two major components and reveals the presence of three others. Some substances may be identified by chromatographic comparison with pure samples.

A. A. ELDRIDGE

2824. **The advantages of matched high-capacity solvents in two-dimensional chromatography.** A. M. Crestfield and F. W. Allen (Univ. Calif., Berkeley, U.S.A.). *Chromatog. Methods*, 1957, **2** (1), 9–11.—A *M* dimethylamine soln. containing 2·4% of adenylic acid, 2% of Na guanylate, 2·3% of cytidylic acid and 2·1% of uridylic acid was chromatographed on Whatman No. 1 filter-paper with *iso*-butyric acid - 0·5 *M* aq. NH_3 (10:6) (**I**) as the solvent for the first-dimensional run, followed by descending chromatography with *iso*propyl alcohol - acetic acid - H_2O (6:3:1) (**II**) or *tert.*-amyl alcohol - H_2O - formic acid (6:3:1) (**III**) as the second solvent. **I** showed excellent capacity, and **III** had a higher capacity than **II**. The use of **I** followed by **III** gave spots with compact shapes.

CHEM. ABSTR.

2825. **Paper-chromatographic separation of hydrophobic substances with cellulose ester paper.** F. Micheel (Inst. of Org. Chem., Wilhelm Univ. Münster, Westf., Germany). *Acta Chim. Acad. Sci. Hung.*, 1957, **12** (3–4), 331–345 (in German).—Acetyl-, butyryl-, benzoyl- and palmitoyl-cellulose papers are used in the chromatographic separation of hydrophobic substances; dimethylaminoacetyl- and trimethylaminoacetyl-cellulose may be used for anion exchange, and phthaloyl- and diacetyl-D-tartaroyl-cellulose for cation exchange (*cf.* Micheel and Albers, *Anal. Abstr.*, 1956, **3**, 3498). Brief directions are given for the preparations of acetyl-cellulose paper. The following mixtures have been successfully analysed—sugar acetates, phenols, Cellitone Fast dyes, aromatic amines, the 2:4-dinitrophenyl derivatives of aliphatic amines, bile acids, male and female sex hormones, fatty acids and their hydroxamic derivatives, and basic amino acids.

A. R. ROGERS

2826. **Chromatographic semi-micro analysis of gases. XV. Automation of the measuring unit of a gas-chromatography apparatus.** J. Janák and K. Tesařík (Lab. Anal. Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (11), 2048–2054.—A new modification is described for the automatic registration of the direct measurement of the vol. of the gas fraction at constant pressure.

J. ZÝKA

2827. **Infra-red indication in gas chromatography.** B. Sekerka, A. Spěvák and K. Friedrich (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Prûmysl*, 1957, **7** (11), 602–604.—Results of the application of thermistors to the indication of the i.r. absorption of the components of mixtures, separated by means of gas - liquid partition chromatography, are discussed.

J. BÖSWART

2828. **Ionisation gauge detector for gas chromatography.** S. A. Ryce and W. A. Bryce (Univ. of British Columbia, Vancouver). *Canad. J. Chem.*, 1957, **35** (11), 1293–1297.—An ionisation gauge is modified as a detector by diverting through it, by means of an adjustable leak, a very small fraction of the gas stream from the chromatographic column. The p.d. between the filament and grid is adjusted to approx. 18 V, a value insufficient to ionise the helium. Substances of lower ionisation potential form ions whose current is amplified and recorded. A linear relationship between peak height and pressure in the gauge is obtained over the range 0·02 to 1·5 mm (Hg). Variation of the flow rate through the gauge from 13% to 0·5% of the flow through the column (38 ml per min.) at 0·7 mm (Hg) does not affect the peak areas. The gauge shows high sensitivity and rapid response.

P. M. SORGO

2829. **Vapour-phase chromatography. II. Quantitative analysis by the use of a laboratory-made apparatus.** Tomio Fukuda, Hisatsugu Omori and Tokishige Kusama (Dept of Ind. Chem., Fac. of Engng, Yokohama Univ., Minami-ku). *Japan Analyst*, 1957, **6** (10), 647–650.—A simple apparatus was made, based on that of Phillips (*J. Chem. Soc.*, 1955, 1480), and its use for the analysis of town gas, cracking gas and an aromatic mixture was examined. Even without the aid of an attachment to keep constant the rate of flow of the carrier gas (N, 5 ml per min.), the voltage of the cell for thermal-conductivity measurement (5·0 V) and the temp., an accurate (error < 1%) analysis could be made by careful observation during the procedure.

K. SAITO

2830. **Sonic gas analyser for measurements of carbon dioxide in expired air.** F. D. Stott (M.R.C., Stoke Mandeville Hospital, Aylesbury, England). *Rev. Sci. Instrum.*, 1957, **28** (11), 914–915.—The instrument described is designed for continuous sampling at a rate of about 2 litres per min. and is intended for the physiological range (0 to 10%) of CO_2. A resonant cavity is maintained in oscillation by a transistor amplifier; the change in frequency caused by CO_2 is linearly related to the CO_2 content.

G. SKIRROW

2831. **Improvements in or relating to [the elimination of standing waves] from sonic gas analysers.** Sir Howard Grubb Parsons & Co., Ltd. [Inventors: A. E. Martin and D. Mounfield]. Brit. Pat. 792,986; date appl. 17.11.54.—The effect of standing waves in a sonic or acoustic gas analyser is inhibited by passing the sound from the transmitter into a continuous annular space so as to travel by separate paths to actuate two microphones, one path being by way of a sample gas and the other by way of a datum gas, *e.g.*, CO_2-free air.

J. M. JACOBS

2832. **Modified form of the constant-volume gas analysis apparatus.** W. J. Gooderham (North Thames Gas Board, London, England). *Chem. & Ind.*, 1957, (46), 1505–1507.—Drawings are shown of an apparatus that combines the best features of the four forms of const.-vol. gas analysis apparatus described previously (Gooderham, *J. Soc. Chem. Ind.*, 1938, **57**, 388T; Edgcombe, *Fuel*, 1946, 163

Flint *et al.*, *B.C.U.R.A. Inform. Circ.* 80, 1953; and S.E. Gas Board, *Standard Methods*). The main advantages claimed are listed; the only disadvantage is in the operation of the Clifton pump.
W. J. BAKER

2833. **Apparatus for measuring the moisture content of sand or the like.** Lime-Sand Mortar Ltd. [Inventor: G. E. P. Jackson]. Brit. Pat. 792,001; date appl. 24.1.55.—The moisture content of sand in bulk in a container is determined by mounting two or more pairs of electrodes in the container, the electrodes of each pair being disposed at a specific distance apart from one another in the body of the sand. By means of switches, each pair of electrodes can be selectively connected with a source of current supply and a current-measuring instrument. It has been found that when the grading of sand of any particular constitution and its degree of compaction remain constant, the resistance to the passage of an electric current through the sand will depend on its moisture content. By measuring this resistance between the pair of electrodes the moisture content can be determined.
J. M. JACOBS

2834. **Laboratory solvent-extraction apparatus.** W. P. Kemp and K. W. Ponting (Thorium Ltd., Uphall Rd., Ilford, Essex, England). *Chem. & Ind.*, 1957, (46), 1504.—The two devices described and illustrated are (*i*) an all-glass settler, consisting of three concentric tubes, for use in counter-current solvent extraction (*cf. Anal. Abstr.*, 1956, **3**, 2579), and (*ii*) an all-glass constant-delivery arrangement comprising an inverted flask, into the ground-glass joint of which is fitted a hollow glass stopper with attached capillary jet and head-control tube.
W. J. BAKER

2835. **A laboratory water separator.** H. Davidge (British Oxygen Res. and Devel. Ltd., Deer Park Rd, London, S.W.19). *Chem. & Ind.*, 1957, (46), 1507.—The arrangement described and illustrated permits the removal of H_2O during esterification and other organic reactions for which the Dean and Stark distillation head is impracticable, *viz*, when the solvent b.p. is $> \simeq 120°$. A one-piece condenser and separator fits into the neck of the reaction flask, the vapours from which are condensed so that the condensate drops into an annular separator where the H_2O collects and the solvent overflows for return to the flask. An annular space ensures cold separation of the solvent - water mixture.
W. J. BAKER

2836. **A vacuum multi-fraction collector.** N. W. Jacobson and J. Miller (Univ., Nedlands, Western Australia). *Chem. & Ind.*, 1957, (50), 1621.—The apparatus described and illustrated is particularly suitable for distilling substances that are viscous liquids or solids at normal temp. Its dimensions are approx. 11 in. by 5 in., and there is provision for seven collectors (5 in. × 0·63 in.), each of which can be easily changed without breaking the vacuum.
W. J. BAKER

See also Abstract—**2602**, Apparatus for analysis of mixtures of O, N and A.

Optical

2837. **'Single addition method' in trace spectral analysis. I. Application to quantitative determinations.** J. Świętosławska and S. Held (Dept. of Tech. Phys., Inst. of Gen. Chem., Warsaw). *Roczn. Chem.*, 1957, **31** (4), 1345–1347.—The method is proposed for use when a standard base entirely free from the element being determined is not available. It is assumed that the relation between line intensity and element concn. is $I = aC^b$ for concn. range 0 to $(x + z)$, the coeff. a and b being constant; b must be known and can be calculated by the method of Gillis and Eeckhout (*Spectrochim. Acta*, 1953, **5**, 409). The required concn., x, is given by $x = z\{(I_{x+z}/I_x)^{1/b} - 1\}^{-1}$, where I_x is the intensity for the sample and I_{x+z} the intensity for the sample with the addition z. The optimum range for (I_{x+z}/I_x) is 2·5 to 1·8. The use of a single addition reduces systematic errors. The accuracy depends on accidental errors and is rather low.

II. Application of linear extrapolation to semi-quantitative determinations. J. Świętosławska and S. Held. *Ibid.*, 1957, **31** (4), 1349–1351.—Unless the value of b in $I = aC^b$ is known, a quant. determination of the concn. cannot be made. For the purpose of a satisfactory semi-quant. determination, the uncorrected concn., x, is given by $x = z\{(I_{x+z}/I_x) - 1\}^{-1}$. The real value of the concn., x_r, is such that $x_{\text{max.}} \leqslant x_r \leqslant x_{\text{min.}}$, where $x_{\text{max.}} = x[100^2/(B_I^- + 100)(B_S^- + 100)]$, and $x_{\text{min.}} = x[100^2/(B_I^+ + 100)(B_S^+ + 100)]$, B_I^+ and B_I^- are the max. positive and negative accidental errors in the determination of the intensities; B_S^+ and B_S^- are the positive and negative systematic errors due to the unknown value of b. The optimum range for I_{x+z}/I_x is 2·5 to 1·8.
T. M. M.

2838. **Method of determining concentration by use of spectral lines in different parts of the spectrum.** I. I. Ezhik and I. A. Kovalev (Kharkov Structural Engng Inst.). *Zavod. Lab.*, 1957, **23** (11), 1355–1357.—In the determination of Na and K by means of an a.c. arc, the lines K 4044·1 A and Na 3302·3 A can be used if a correction based on the contrast factor (γ) values of the plate in these two regions is made. For this purpose the lines of Cu 4022·7 and 3290·5 A that appear when copper electrodes are used are measured.
G. S. SMITH

2839. **Spectrographic analysis with a single calibration curve by the method of independent evaporation in an atmosphere of chlorine.** I. M. Kustanovich (Magnitogorsk Ind. Tech. School). *Zavod. Lab.*, 1957, **23** (11), 1332–1335.—Apparatus for arc excitation of ores and ferrous alloys in a current of Cl is described. The method eliminates the effects of sample composition and structure on spectrographic results.
G. S. SMITH

2840. **Determination of the "effective width" of lines in the analysis [spectrographic] of powdered substances.** A. Fiorenza and M. Lachin (Lab. Gomma, Pirelli S.p.A. Milano, Italy). *Spectrochim. Acta*, 1957, **10** (1), 85–98 (in French).—The difficulties of applying spectrographic analysis to the determination of the constituents of powders are discussed and the advantages of measuring line widths rather than densities are reviewed. It is advisable to measure a group of lines rather than a single one. The special photometer required for measuring line widths is described. The method has been applied to the analysis of ash, especially from some ingredients used in the rubber industry.
K. A. PROCTOR

2841. **Use of a quartz spectrograph as a monochromator.** S. Z. Shul'ga (Inst. of Physics, Acad. Sci., UkrSSR). *Zavod. Lab.*, 1957, **23** (11), 1385–1386.—Modifications to a Hilger-type spectrograph are described.
G. S. SMITH

2842. **Apparatus for spectro-titration of sub-milligram samples.** H. E. Boaz and J. W. Forbes (Eli Lilly and Co., Indianapolis, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 456.—The accessory described for the Cary Model 11 spectrophotometer makes it possible to change the pH over the range 0·5 to 13·5 whilst the cell remains in position in the instrument; the u.v. spectrum can thus be continuously observed.
K. A. PROCTOR

2843. **High-precision photo-electric polarimeter.** E. J. Gillham (Light Div., Nat. Phys. Lab., Teddington, England). *J. Sci. Instrum.*, 1957, **34** (11), 435–439.—The instrument is designed for standardisation work on quartz control-plates. A revolving disc carries segments of optically active quartz, which cause the plane of polarisation of the light incident on the analyser to alternate between two positions at low audio-frequency. The setting position of the analyser is that in which the intensity of the emergent light, as indicated by means of a photomultiplier and amplifier, is unmodulated.
G. SKIRROW

Thermal

2844. **Determination of the boiling-points of organic liquids by means of a simple ebulliometer.** L. A. Mikhallova and M. Z. Partashnikova (Sci. Res. Inst. of Chem. Reagents). *Zavod. Lab.*, 1957, **23** (11), 1388–1391.—Apparatus is described.
G. S. SMITH

2845. **The ebullioscopic micro-determination of molecular weight. An improved micro form of the Menzies - Wright ebulliometer.** A. F. Colson (I.C.I. Ltd., Res. Dept., Alkali Div., Northwich, Cheshire, England). *Analyst*, 1958, **83**, 169–176.—The micro-ebulliometer is described in detail. Heat is supplied by a gas micro-burner and the elevation of b.p. of the solvent is measured by means of a differential water thermometer. The solvents used are benzene, CCl_4 and abs. ethanol. To determine the constant of the instrument, the solvent is boiled until the differential thermometer (read with a cathetometer) indicates a constant temp., a known wt. of pure dry benzil is introduced, and the thermometer reading is recorded. The b.p. of the solvent is determined separately with a mercury thermometer in the vapour of the boiling liquid. The constant of the instrument is then calculated from the observed elevation of b.p. and the mol. wt. of benzil. To determine the mol. wt. of the sample, the "zero" thermometer reading, the elevation of b.p. and the b.p. of the solvent are determined as before. Expressed as coeff. of variation, the accuracy and precision of the method for mol. wt. in the region of 200 are 1·8 and 1·3, respectively, with benzene as solvent, and 2·3 and 2·1%, respectively, with CCl_4 as solvent. The instrument cannot be used with solvents of b.p. $> 80°$.
A. O. JONES

2846. **Continuous-recording laboratory thermo-balance.** E. S. Bartlett and D. N. Williams (Non-ferrous Phys. Metall. Div., Battelle Memorial Inst., Columbus, Ohio). *Rev. Sci. Instrum.*, 1957, **28** (11), 919–921.—The instrument's sensitivity permits measurement of weight-change rates of 3 to 70 mg per min. The change in weight is determined by a strain-gauge wire.
G. SKIRROW

2847. **Gas indicator.** J. Fiehman (Chem. Lab., Acad. Sci., Prague). *Chem. Průmysl*, 1957, **7** (11), 605–606.—The method is based on the indirect measurement of thermal conductivity and the comparison of thermal conductivities of two different gases. By assuming that the interfering influence of other gases and vapours is limited, the indicator may be used for practically every range of measured concn. of two gases with adequately differing thermal conductivities.
J. BÖSWART

2848. **Apparatus for thermal analysis.** M. Thomas. *Chim. Anal.*, 1957, **39** (11), 404–412.—An apparatus is described and illustrated for which improved precision is claimed in the determination of "temperatures of complete fusion" (T.F.F.) and "temperatures of commencing crystallisation" (T.C.C.). The appropriate time - temperature curves are plotted, and the T.C.C. is derived from the cooling-curve by the method of Moulin (*J. Chim. Phys.*, 1910, **8**, 321), the T.F.F. being obtained as the intersection of tangents to the two portions of the heating-curve before and after the T.F.F. The manipulation of the apparatus is described, and factors affecting the precision of the results are studied; these include the difference in temperature between the jacket and the T.C.C. or T.F.F., the rapidity of stirring, the influence of superfusion, and the thermometer corrections. The apparatus can be used for cryometry at elevated temperatures, and for the precise determination of solubility - temperature curves.
R. E. ESSERY

See also Abstract—**2578**, Vacuum-fusion apparatus.

Electrical

2849 **Simple assembly for paper electrophoresis** C. F. Walter and R. S. Ingols (Inst. of Technol. Atlanta, Georgia, U.S.A.). *Chemist Analyst*, 1957 **46** (4), 103.—The apparatus described is made from polyethylene boxes of a type commercially available in the U.S.A.
G. S. ROBERTS

2850. **Square-wave polarograph.** R. E. Hamm (Univ. of Utah, Salt Lake City, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 350–354.—The instrument described was designed and constructed so that the fundamentals of the method could be studied, and its characteristics have been determined for several inorganic ions. It is less sensitive than the Barker square-wave polarograph (*Analyst*, 1952, **77**, 685) but its resolution is approx. the same.
K. A. PROCTOR

2851. **The use of a polarograph for potentiometric pH determinations.** E. Macovschi and D. Motoc Grigoraş (Inst. für Biochem., Akad. der Rumänischen Volksrepublik). *Rev. Chim., Romania*, 1951 **2** (2), 293–298 (in German).—An arrangement is described in which a polarograph is used to record the balance point of a potentiometric circuit in pH determinations. The modified circuit, in which the usual Weston cell is replaced by a polarograph circuit, is shown diagrammatically. The balance point is first roughly estimated, and then the changes in this region are recorded by means of the polarograph. The method was tested by a series of experiments with various voltages and buffer solutions. Results are detailed. The method has the following advantages—(*a*) greater accuracy than conventional polarographic methods for the determination of pH

(*b*) applicability to non-buffered soln., (*c*) applicability over the whole pH range 0 to 14 by choice of suitable electrodes, (*d*) the use of a dropping mercury electrode is eliminated, (*e*) results are registered automatically and permanently, and (*f*) pH values of the soln. under investigation can be obtained immediately before and after polarography without emptying the cell or using a special potentiometer.

S. M. MARSH

2852. **Electrometric pH measurements under extreme conditions. I. Measurement of hydrogen ion concentration in strongly acid and alkaline solutions.** K. Schwabe (Tech. Hochschule, Dresden). *Chem.-Ing.-Tech.*, 1957, **29** (10), 656–660.—The use of glass electrodes for measuring the pH of strongly acid or alkaline soln. is described, with particular reference to special alkali-resistant glasses. Diffusion potentials in salt bridges are discussed. The pH can be determined by titration, by direct measurement of the H^+ or OH^- concn. or by conductivity measurements. The effect of salts on the activity of the hydrogen ion is considered.

A. B. DENSHAM

2853. **Coulometric determinations.** F. Čůta (Inst. of Chem. Technol., Prague). *Anal. Chim. Acta*, 1958, **18** (1–2), 45–50 (in English).—The technique of coulometric titrations is briefly summarised under the headings of coulometry at constant current and coulometry at constant potential. Some indication is given of their wide application. The precision of such titrations is at least as good as that of volumetric titrations.

J. H. WATON

2854. **Potentiometric method of analysis with rotating platinum-wire electrode. I. Fundamental characteristics of rotating platinum-wire electrode in practical use.** Jinzo Hashimoto (Chem. Dept., Fac. of Sci., Tokyo Univ. of Education, Koishikawa). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (12), 1726–1728.—Attempts were made to elucidate the source of insufficient reproducibility of a rotating platinum-wire electrode. The rate of potential change must be reduced with decreasing rate of revolution (1·2 mV per sec. for 815 r.p.m.; 0·9 mV for 600 r.p.m.; 0·25 mV for 175 r.p.m.) for a reproducible current - potential diagram to be obtained. Preliminary electrolysis in 10 *N* HNO_3 at +0·1 to 0·2 V (*vs.* the mercury cathode) makes the surface of the platinum suitable for potentiometric use.

II. Current equation for the rotating platinum-wire electrode. Jinzo Hashimoto. *Ibid.*, 1957, **78** (12), 1729–1732.—The limiting current (*i*) with a rotating platinum-wire electrode (*N* r.p.m.) is discussed theoretically and the following formula is obtained—$i = knFCAD^{2/3}N^{1/2}$, where k is a const., n is the charge of the ion, C is the concn. of the ion to be reduced, A is the area of the electrode, and D is the diffusion coeff. The validity of this formula was examined with I^-, Br^- and $Fe(CN)_6^{4-}$.

K. SAITO

2855. **Potentiometry at constant intensity.** R. Gauguin (Centre de Recherches, Cie Pechiney, Aubervilliers, France). *Anal. Chim. Acta*, 1958, **18** (1–2), 29–39 (in French).—Potentiometry at constant current is a generalisation of classical potentiometry, and has the advantage that it admits of potentiometric methods for the detection of the end-point, even with material that is scarcely electro-active. The shape of the titration curve, as well as the conditions necessary for the detection of the end-point with a given precision, may be forecast from a study of the polarisation curves. The high resistance in the electrolysis circuit is of great importance, since there is a progressive change from potentiometric to amperometric curves as its value decreases. Titrations in which this technique is used are readily made automatic.

J. H. WATON

2856. **Chronopotentiometric studies at solid electrodes.** R. N. Adams, J. H. McClure and J. B. Morris (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 471–475.—The anodic oxidation of aromatic amines and phenols at platinum electrodes has been studied and $E_{\frac{1}{4}}$ values *vs.* the S.C.E. are given for a variety of compounds as a function of pH, substitution, etc. With the simple apparatus described, this appears to be a promising technique for rapid, routine analysis, and has been applied to the oxidation reactions of hydrazine and substituted hydrazines, antioxidant molecules such as tetramethyl-*p*-phenylenediamine and thiols, and some mercapto compounds such as cysteine and thiouracil.

K. A. PROCTOR

2857. **Chronopotentiometry in fused lithium chloride - potassium chloride.** H. A. Laitinen and H. C. Gaur (Noyes Chem. Lab., Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1958, **18** (1–2), 1–13 (in English).—Chronopotentiometric studies were carried out for the reduction of the chlorides of Cd, Co, Pb and Tl^I in a fused eutectic mixture of KCl and LiCl at 450°. Transition times were kept to <1 sec., and the potential - time curve was recorded oscillographically. Linear diffusion occurs for electrodes whose dimensions are much greater than the thickness of the diffusion layer.

J. H. WATON

2858. **Amperometry with two indicator electrodes.** H. L. Kies (Anal. Chem. Lab., Tech. Hoogschool, Delft, Holland). *Anal. Chim. Acta*, 1958, **18** (1–2), 14–28 (in French).—The titration curves obtained when the dead-stop procedure is used are explained from a consideration of the polarisation curves. A brief review covers the work already published, and further applications of the dead-stop procedure are given.

J. H. WATON

2859. **A new high-frequency titrimeter with a magnetic core.** Kunio Nakano, Setsuko Shibata and Akito Satsuka (Fac. of Sci., St. Paul Univ., Ikebukuro, Toshima-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (9), 1421–1422.—For an improved high-frequency titration by the use of a secondary current (Nakano *et al.*, *Ibid.*, 1954, **75**, 776; 1956, **77**, 551, 1626, a closer coupling of the secondary current is effected by means of a magnetic core inserted into the sample soln. The downward slope of the "fundamental curve" (*loc. cit.*) obtained by this titrator gradually increases in $>0·1$ *M* soln. of the electrolyte without max. or min. A peak due to condenser action, which is seen in very dil. soln. with the ordinary high-frequency titrimeter, does not appear. The defects involved in high-frequency titration appear to be eliminated.

K. SAITO

2860. **High-frequency titrimetry. Use for titrations in anhydrous medium.** Y. Conseiller and J. Courteix (Soc. des Usines Chimiques, Rhône-Poulenc, France). *Anal. Chim. Acta*, 1958, **18** (1–2), 166–173 (in French).—A high-frequency titration

apparatus, stabilised by a quartz piezo-electric crystal, is described. By this means, organic bases in glacial acetic acid are determined on the semi-micro scale. J. H. WATON

2861. **Possibilities of applying high-frequency measuring technique in analytical chemistry.** F. Oehme (Inst. Mikrobiol. u. exp. Therapie, Jena, Germany). *Anal. Chim. Acta*, 1958, **18** (1–2), 155–165 (in German).—Single-stage quartz oscillators can be used to determine dielectric constants, dielectric losses and high-frequency conductivities by the compensation or deflection methods. After a description of suitable cells, some analytical applications of the high-frequency technique are listed. J. H. WATON

2862. **Technique of the isotope dilution method.** G. N. Bilimovich and I. P. Alimarin (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1957, **12** (6), 685–689.—Isotope dilution can be used to determine elements by means of reactions that do not give quant. separations. The principles of the method and apparatus used, together with applications to the determination of Bi and Pb by means of ^{210}Bi and ^{212}Pb, are described. G. S. SMITH

2863. **The development of gamma-ray spectrometry applied to the analysis of radio-isotopes.** D. H. Pierson and P. Iredale (A.E.R.E., Berks., England). UNESCO/NS/RIC/53, 1957, 9 pp.—The use of a two-crystal Compton subtraction spectrometer (*cf. Anal. Abstr.*, 1957, **4**, 1092) with a multi-channel pulse amplitude analyser is described. By means of a single sodium iodide crystal of 3 in. diam. and 3 in. height with the analyser, individual activities of the order of 10^{-11} C have been measured in 16 hr. A resolution of 6% for 60 keV γ-rays has been obtained with a xenon-filled proportional counter; by measuring the Ba 31·9 keV X-ray with such a counter it has been possible to determine ^{137}Cs - ^{137}Ba in the presence of four times as much ^{95}Zr - ^{95}Nb. G. J. HUNTER

2864. **Low-voltage techniques in high-molecular-weight mass spectrometry.** H. E. Lumpkin (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 321–325.—The mass spectra of molecules containing double bonds can be greatly simplified by lowering the ionisation voltage so that the energy available is sufficient to form the molecule ion, but is too low to form fragment ions. This technique, for which calibration data and examples are given, simplifies the interpretation of the spectra of the higher boiling ranges of petroleum. The lack of stability of instrument sensitivity may present a problem at such low-voltage operations. K. A. PROCTOR

2865. **Application of total ionisation principles to mass-spectrometric analysis.** G. F. Crable and N. D. Coggeshall (Gulf Research and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 310–313.—An equation that has been derived from the work of Otvos and Stevenson (*J. Amer. Chem. Soc.*, 1956, **78**, 546) predicts that total ionisation data for homologous hydrocarbon series will form a family of parallel straight lines when plotted as a function of mol. wt. Experimental data substantiate this prediction. K. A. PROCTOR

2866. **Mass-spectrometer ionisation chamber.** J. A. Rickard (Humble Oil & Refining Co., Houston, Texas). *Rev. Sci. Instrum.*, 1957, **28** (11), 967–968.—Two ion sources are described; in both the magnets and the appropriate pole pieces are integral with the ionisation chambers. The design described is claimed to facilitate the alignment of the magnetic field and permits adjustment of the ion-source position for an optimum ion-beam focus while the proper electron-beam alignment is automatically maintained. By using a double ion-beam collector and standard reference sample, a precision of ± 0·01% is claimed for the determination of the isotopic ratio of ^{12}C and ^{13}C. G. SKIRROW

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_B
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

apparatus, stabilised by a quartz piezo-electric crystal, is described. By this means, organic bases in glacial acetic acid are determined on the semi-micro scale. J. H. WATON

2861. **Possibilities of applying high-frequency measuring technique in analytical chemistry.** F. Oehme (Inst. Mikrobiol. u. exp. Therapie, Jena, Germany). *Anal. Chim. Acta*, 1958, **18** (1–2), 155–165 (in German).—Single-stage quartz oscillators can be used to determine dielectric constants, dielectric losses and high-frequency conductivities by the compensation or deflection methods. After a description of suitable cells, some analytical applications of the high-frequency technique are listed.
J. H. WATON

2862. **Technique of the isotope dilution method.** G. N. Bilimovich and I. P. Alimarin (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1957, **12** (6), 685–689.—Isotope dilution can be used to determine elements by means of reactions that do not give quant. separations. The principles of the method and apparatus used, together with applications to the determination of Bi and Pb by means of ^{210}Bi and ^{212}Pb, are described. G. S. SMITH

2863. **The development of gamma-ray spectrometry applied to the analysis of radio-isotopes.** D. H. Pierson and P. Iredale (A.E.R.E., Berks., England). UNESCO/NS/RIC/53, 1957, 9 pp.—The use of a two-crystal Compton subtraction spectrometer (*cf. Anal. Abstr.*, 1957, **4**, 1092) with a multi-channel pulse amplitude analyser is described. By means of a single sodium iodide crystal of 3 in. diam. and 3 in. height with the analyser, individual activities of the order of 10^{-11} C have been measured in 16 hr. A resolution of 6% for 60 keV γ-rays has been obtained with a xenon-filled proportional counter; by measuring the Ba 31·9 keV X-ray with such a counter it has been possible to determine ^{137}Cs - ^{137}Ba in the presence of four times as much ^{95}Zr - ^{95}Nb. G. J. HUNTER

2864. **Low-voltage techniques in high-molecular-weight mass spectrometry.** H. E. Lumpkin (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 321–325.—The mass spectra of molecules containing double bonds can be greatly simplified by lowering the ionisation voltage so that the energy available is sufficient to form the molecule ion, but is too low to form fragment ions. This technique, for which calibration data and examples are given, simplifies the interpretation of the spectra of the higher boiling ranges of petroleum. The lack of stability of instrument sensitivity may present a problem at such low-voltage operations.
K. A. PROCTOR

2865. **Application of total ionisation principles to mass-spectrometric analysis.** G. F. Crable and N. D. Coggeshall (Gulf Research and Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 310–313.—An equation that has been derived from the work of Otvos and Stevenson (*J. Amer. Chem. Soc.*, 1956, **78**, 546) predicts that total ionisation data for homologous hydrocarbon series will form a family of parallel straight lines when plotted as a function of mol. wt. Experimental data substantiate this prediction.
K. A. PROCTOR

2866. **Mass-spectrometer ionisation chamber.** J. A. Rickard (Humble Oil & Refining Co., Houston, Texas). *Rev. Sci. Instrum.*, 1957, **28** (11), 967–968.—Two ion sources are described; in both the magnets and the appropriate pole pieces are integral with the ionisation chambers. The design described is claimed to facilitate the alignment of the magnetic field and permits adjustment of the ion-source position for an optimum ion-beam focus while the proper electron-beam alignment is automatically maintained. By using a double ion-beam collector and standard reference sample, a precision of ± 0·01% is claimed for the determination of the isotopic ratio of ^{12}C and ^{13}C. G. SKIRROW

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_{B}
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

Volume 5. No. 8, Abstracts 2478-2866 August, 1958

ANALYTICAL ABSTRACTS

A PUBLICATION OF
THE SOCIETY FOR ANALYTICAL CHEMISTRY

CONTENTS

Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England.
Communications to be addressed to the Editor, Norman Evers, 14, Belgrave Square, London, S.W.1.
Enquiries about advertisements should be addressed to Walter Judd Ltd., 47, Gresham Street, London, E.C.2.
Entered as Second Class at New York, U.S.A., Post Office